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REPORT OF THE SEMINAR ON METHODS OF DETECTION, MEASUREMENT AND MONITORING OF POLLUTANTS IN THE MARINE ENVIRONMENT

Rome, 4 - 10 December 1970

Supplement to the Report of the

TECHNICAL CONFERENCE ON MARINE POLLUTION AND ITS EFFECTS ON LIVING RESOURCES AND FISHING

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FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS
ROME, 1971

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Organized by FAO with the support of Unesco, IAEA, SCOR and WMO

Rome, 4-10 December 1970

SUPPLEMENT TO THE

REPORT OF THE TECHNICAL CONFERENCE ON MARINE POLLUTION AND ITS EFFECTS ON LIVING RESOURCES AND FISHING

Prepared by

Fishery Resources Division
Department of Fisheries

FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS
Rome, August 1971

PREPARATION OF THIS REPORT

The volume contains the revised and amended version of the original Report of the Seminar on Methods of Detection, Measurement and Monitoring of Pollutants in the Marine Environment (FIR:TPME/70/6 Rev., 9 December 1970). This Seminar was held in Rome, 4-10 December 1970, as a special session of the FAO Technical Conference on Marine Pollution and its Effects on Living Resources and Fishing. In consultation with the Convener of the Seminar, Dr. E.D. Goldberg, the Report was compiled and edited by Dr. G. Tomczak of the Marine Biology and Environment Branch of the Fishery Resources Division who acted as the Secretary of the Seminar.

The views expressed in the Report are those of the Seminar participants and are not necessarily those of FAO and other supporting agencies (Unesco, IAEA, SCOR and WMO).

It is contemplated to produce, through SCOR, as one of the sponsoring bodies, an expanded edition as "A Guide to Marine Pollution", using the documentation prepared for the Seminar and the relevant sections of the Report. This book will be published by Gordon and Breach, Science Publishers, Inc., New York.

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INTRODUCTION

Edward D. Goldberg
(Convener)

The future consequences of society's debauchery of the environment are viewed in a variety of ways. The so-called "jeremiahs of science" predict in the public press and over radio and television, on the bases of losses of natural resources and the mass mortalities of living creatures, the extinction of the human race. Other scientists show little concern for environmental alterations and insist that the powers of technology can overcome any inconveniences resulting from the dispersions of man's wastes. In addition, some of the younger generation have lost respect for social systems that do not provide prompt and decisive countermeasures to environmental insults.

Yet, those in public office, responsible for the management of our surroundings do rely upon specialists from the scientific community to define critical environmental problems and to provide alternate courses of action to minimize the deleterious effects of man's impingements. It was to this end that FAO assembled during the first week of December 1970 forty of the world's distinguished environmental and natural scientists to identify materials posing threats to the marine environment and to critically appraise the existing methods for their detection, measurement and monitoring. Further, research needs for developing and improving analytical techniques were to be delineated.

The participants were distributed into nine panels, seven concerned with various groups of pollutants, one with the use of marine organisms to assess contamination levels and one with the establishment of baseline and monitoring systems. The combined results of the deliberations will provide direction for the training of technical personnel and management involved in marine pollution problems.

The world scientists are now ready to measure the health of the oceans. The assemblage of methods for many of the substances introduced to the seas in substantial quantities by the activities of man offers a springboard for a baseline survey to establish their concentrations in the waters, organisms and sediments of the sea. All of the panels emphasized the need for such knowledge. If one couples the proposed 1 000-sample programme designed at Williamstown, Massachusetts, in 1970 with these techniques, an investigation can be initiated immediately. The results of such a study are absolutely essential before monitoring programmes, that will follow long-term trends or that will document disaster, are begun.

The Seminar delineated an urgent requirement for the gathering of data on the world production of both organic and inorganic chemicals as a guide to evaluate their potential dangers to the environment. In addition, the knowledge of the paths of consumption and disposition, where known, will substantially aid the assignment of priorities for the development of analytical techniques or for the formulation of survey programmes defining their oceanic dispositions. The Seminar urges the establishment of a Document Centre to handle such information. Further, a citation index indicating the appearances of man-produced substances in the marine environment could be accommodated in such an institution.

The formulation of analytical techniques for pollutants in the marine environment has gone hand in hand with the adoption of regulations controlling their releases to the environment. Substances are identified as being dangerous primarily upon the basis of their possible deleterious effects to man and acceptable levels in water or in organisms of the sea are established. Subsequently laws or policies controlling the environmental dispersion of these materials evolve.

Such has been the case with the radio-active wastes. As a result of the detonations of nuclear devices and of the prospect for more and more fission reactors, hazards that could arise from the uncontrolled dispersion of nuclear wastes were identified. Acceptable levels for the waters, plants, and animals of the sea were developed on the basis of potential dangers to man through his ingestion of seafoods. As a result, discharges of nuclear wastes have been regulated, and the dumping of high level radio-activities to the oceans has been prohibited. The management of nuclear débris has reached such an effective state that the Panel on Radio-activity submits that in the continued absence of extensive nuclear testing there will most probably be a decrease in the oceanic standing crop of artificial radio-active substances during the forthcoming years even though there will be a marked increase in nuclear reactors.

Analytical techniques for other man's wastes entering the oceans such as the halogenated hydrocarbon pesticides and their residues and mercury are evolving in similar ways. Regulatory actions restricting either the environmental dissemination of these materials or their levels in food products are gradually being adopted in some countries. The pressures to develop sensitive and reliable methods come about when those responsible for the management of our environment need an objective evaluation of existing or potential perils.

The pattern so far developed for the evolution of analytical techniques places a considerable burden upon the scientific community to rapidly identify those materials that can cause perils to our surroundings. Nearly all of the Panels concerned with contaminants identified specific examples of man's waste products which may be leaking to the environment in substantial quantities and for which as yet there are no analytical techniques available.

The Panels were also aware of the difficulties that will arise from the large number of man-introduced materials that are being accumulated in the living organisms of the sea. Dead birds are found to have high contents of mercury, DDT and its residues, and PCB's. Which of these substances acting alone or in combination, have contributed to the fatalities observed?

The seventh decades of the past two centuries have been pioneering periods in marine chemistry. In the 1770s, Antoine Lavoisier in France and Tobern Bergman in Sweden first analysed sea waters. In the 1880s the earth-circling Challenger Expedition collected sea-water samples from many depths and gave a third dimension to the distribution of chemicals in the world ocean. In the 1970s the marine science community is defining the chemical invasion of the oceans by man.

Panel 1: HALOGENATED HYDROCARBONS

R.W. Risebrough (Chairman)
E. Huschenbeth
S. Jensen
J.E. Portmann

1. INTRODUCTION

Halogenated hydrocarbons constitute a class of synthetic chemicals which have come into widespread use in both industry and agriculture. Global production figures for the chlorinated hydrocarbon insecticides are currently in the order of 200 000 tons per year. Production of industrial halogenated hydrocarbons has expanded with the development of a global technology, and current production figures exceed those of the insecticides. The relative chemical stability of many of these compounds and their mobility have resulted in the transfer of a significant fraction of the total production to the marine environment. Large amounts are also transferred to the sea in sewage outfalls and by dumping. Since continued accumulation in the sea constitutes a potential threat not only to marine ecosystems but also to marine food resources, it has become essential to determine the rates of accumulation through the establishment of a monitoring system. In this report we briefly review the state of our current knowledge of the distribution of these pollutants in the sea in an attempt to establish the criteria for a meaningful monitoring programme. We have also attempted to review current methodology and to suggest techniques which might be adopted in a United Nations programme of assistance to developing countries. It should be pointed out, however, that progress in this field is rapid and that methodologies are constantly being revised. A programme is therefore proposed for the calibration of standards and the exchange of samples to ensure that different laboratories obtain equivalent results. We have suggested that the programme retain a certain flexibility in order to respond to changing research needs.

2. CHEMICAL AND PHYSICAL DESCRIPTION OF POLLUTANTS, INCLUDING METABOLISM

Of the halogenated hydrocarbons produced today, the following have so far been detected in the marine environment: aliphatic by-products of vinyl chloride production (AHC), the DDT compounds, polychlorinated biphenyls (PCB), dieldrin, endrin and benzene hexachloride (BHC). Many halogenated hydrocarbons have not yet been looked for in the sea. These include fluorinated and brominated compounds, polychlorinated naphthalenes and their derivatives, dichloroethylene, trichloroethylene, chloroform, carbon tetrachloride, and chlorinated hydrocarbon by-products produced during the synthesis of these and other compounds.

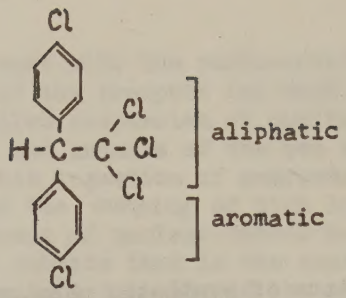
2.1 Aliphatic chlorinated hydrocarbons

The compounds with which the panel is concerned all contain one or more chlorine atoms. Generally, chlorination or fluorination of a hydrocarbon increases the stability of the compound to both chemical and biological degradation. Among the chlorinated hydrocarbons, the aliphatic compounds are usually less stable than the aromatics. The by-products formed in the production of vinyl chloride (Jensen *et al.*, 1970) contain from one to four carbons in the chain and from one to five chlorines per molecule. Generally, they are relatively easily metabolized. AHC are rather low-boiling oils or liquids with boiling points ranging from 83°C at 760 mm Hg (1,2-dichloro ethane) to 67°C at 10 mm Hg (1,2,4-trichloro-2-butene) (Jensen *et al.*, 1970, Table I). The water solubilities are in the range of grams per litre.

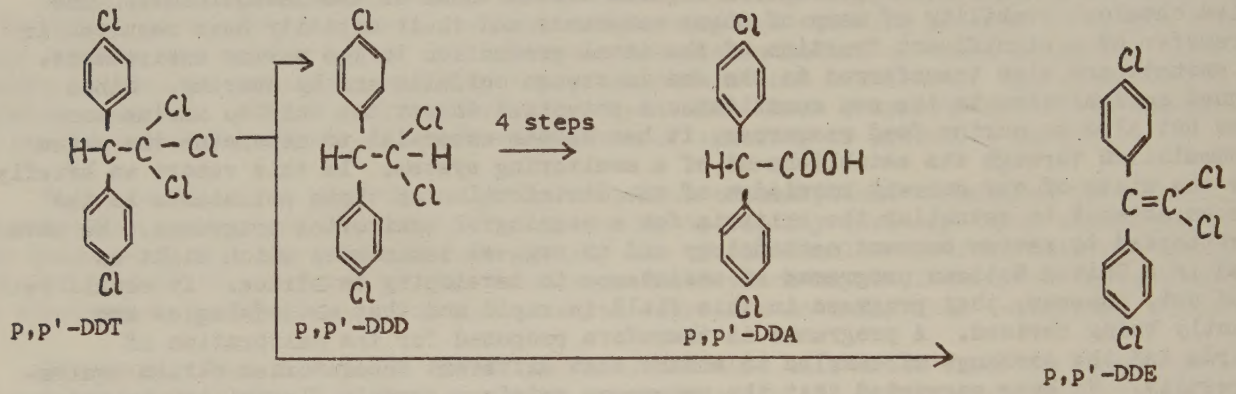
2.2 DDT compounds

When, in addition to aliphatic-bound chlorine, a molecule such as p,p'-DDT also contains chlorinated aromatic groups, the stability to both chemical and biological degradation increases considerably and the half-life time in the environment changes from months to years. The water solubility also decreases and for p,p'-DDT is around 1 µg/l.

p,p'-DDT



The metabolism of p,p'-DDT takes place in the aliphatic part of the molecule and usually proceeds by either of two pathways:

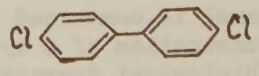


DDE is usually the predominate metabolite in the higher trophic levels, perhaps because DDD can be metabolized to the excretable DDA.

The half-life of p,p'-DDT depends on the medium. There is considerable evidence that in the cold zones of the world in waters poor in nutrients, p,p'-DDT is stable for long periods of time. In these regions p,p'-DDT may be the predominate DDT compound in fish, whereas in warm inland lakes, fish frequently contain only the metabolites DDD and DDE. In soil, residence half-life times up to 10 years have been recorded for p,p'-DDT. DDE is even more stable than p,p'-DDT.

2.3 PCB

Without the aliphatic portion, DDT would be a simple polychlorinated biphenyl molecule.



This molecule is considerably more stable than DDT and the stability increases with the introduction of additional chlorine atoms. There are 210 theoretical homologues and isomers of PCB.

PCB, as used in industry, has a chlorine content ranging from 30% to 60%, depending upon the application, and is a mixture of homologues and isomers. Thus a PCB with 50% average chlorine content consists of biphenyl molecules with 4 to 8 chlorines. If the chlorines are as evenly distributed as possible between the two phenyl groups, there are 104 different PCB molecules. About 14 peaks normally appear on gas chromatograms but because of over-lapping, many more compounds may be present. PCB is an oil with a high solubility in animal lipids. While p,p'-DDT is readily converted to DDE in an alkaline medium, PCB is stable to both strong acid and alkali. If the chlorine number increases above 4, PCB is non-inflammable.

2.4 Aldrin-Dieldrin-Endrin

Aldrin is a chlorinated hydrocarbon which is alicyclic and is therefore less stable to oxidation than the aromatics, being readily converted to the epoxide, dieldrin, which is also used as a pesticide. Further degradation takes place at the epoxide ring to the di-alcohol, but the molecule may also be altered at other sites. Endrin is a stereo-isomer of dieldrin and is one of the more toxic of the pesticides.

2.5 Lindane (gamma-BHC)

This fully chlorinated compound is also alicyclic and may be metabolized in several ways, with one of the dominant transformations yielding the trichlorobenzene. Several stereo-isomers are formed in the production of lindane. The mixture is occasionally used in agriculture, and of the several isomers, the beta-isomer is considerably more stable.

3. HALOGENATED HYDROCARBONS IN THE MARINE ENVIRONMENT

3.1 Distribution of halogenated hydrocarbons in the marine environment

There is now a considerable body of evidence to suggest that some form of equilibrium exists between the level of organo-chlorine pollutants in water and that in marine animals. Reinert (1970) has shown that the levels of pesticides in fish are directly related to the fat content and rise with size of fish only as the fat content increases. Risebrough *et al.*, (1971) were not able to find any relationship between the size of animal and organo-chlorine pesticide concentration, and the panel was not aware of any studies which demonstrated a relationship between organo-chlorine pesticide concentration and size *per se*.

Several workers, e.g. Gakstatter and Weiss (1967), Butler (1969), Alabaster (1970) and Grzenda *et al.*, (1970) have conducted careful studies with fish or oysters held first in organo-chlorine pesticide polluted waters during which their body burdens of organo-chlorines increased, and subsequently in clean waters during which time the body burdens decreased, thus demonstrating that organo-chlorine pesticide concentrations within fish and oysters are related to concentrations in the ambient water. Although marine mammals and sea birds do demonstrate definite food chain concentration effects there is little evidence to suggest that marine fish at higher trophic levels have high organo-chlorine pesticide concentrations purely because of their predatory role. Jensen *et al.* (1969a,b) found higher concentrations of these substances in the Baltic herring than in Baltic cod and attributed this to different concentrations of fat. There is, however, evidence to suggest that concentrations in the diet do influence residue levels.

Very few analyses for organo-chlorine pesticides appear to have been carried out on sea water and the panel considered that present methodology was not capable of detecting, on a routine basis, the quantities of these compounds in open sea waters. The panel also considered that there was little data available regarding the adsorption characteristics of organo-chlorine pesticides on particulate matter. It is, however, known that surface slicks of natural or mineral oil origin do contain concentrations of organo-chlorine pesticides considerably higher than those presumably found in sea water (Seba and Corcoran, 1969). Since levels in sea water are at present not readily detectable the panel considered that in view of the increasing body of evidence suggesting equilibria between fish and water, calculation of concentrations in the water might be possible indirectly by a knowledge of the concentration in marine fish (see section 5).

The panel felt that a knowledge of the concentration of chlorinated hydrocarbons in sediments is essential to the construction of a budget for each compound, since deposition in the sediments is assumed to be a major pathway whereby they leave marine ecosystems. Such studies, however, should be a part of an intensive project undertaken in each area investigated and accomplished within a short time period, along with measurements of other components of the ecosystem. The panel concluded that routine analyses of sediments over extended time periods during a monitoring programme would not yield useful data.

Although data for PCBs is not as complete as for organo-chlorine pesticides the panel felt that by analogy PCBs would probably behave similarly and that concentrations in the marine environment would be governed largely by the partition between fat and water. The aliphatic chlorinated hydrocarbons are in general much more water soluble than the other materials considered by the panel and concentration factors in organisms over sea water are therefore likely to be much lower. Preliminary data suggest a value of up to 200 times rather than 10 000 as for DDT (Jensen et al., 1970).

Of the various chlorinated hydrocarbons considered, the panel considered DDE to be that most ubiquitous. The highest concentrations, such as those found in sea birds from southern California and the Baltic (an average of 1 100 ppm DDE and 200 ppm PCBs in fat from 100 brown pelican eggs off California and 1 000 ppm DDE and 540 ppm PCB in fat from eggs of the white-tailed eagle in the Baltic) appear to be related to the incidental discharge of DDT from manufacturing plants and to industrial use of PCB in nearby areas. Concentrations of pesticides can differ considerably even in adjacent sea areas. Jensen et al. (1969a,b) demonstrated that concentrations of organo-chlorine pesticides and PCBs in fish from the Baltic increased from north to south and in the southern area were approximately 10 times higher than in fish from the nearby Swedish west coast. The panel considered it probable that the concentration of DDE relative to p,p'-DDT might differ considerably in different parts of the world, due to different decomposition rates of p,p'-DDT which are probably highest in eutrophic and tropical areas.

The panel felt that there were many areas of the world where even though pesticide usage was high, data on residues were either totally lacking or very sparse and that there was a strong likelihood that high concentrations would be found in these areas if and when monitoring studies were instituted. The panel also felt that such monitoring studies should initially be orientated so as to check on species of economic importance to developing countries such as shrimps in estuarine environments (see also section 5).

3.2 Transfer of chlorinated hydrocarbons to the marine environment

The potential impact of a pollutant upon a marine community will be determined by the rates of accumulation to a concentration associated with deleterious effects. Global production rates of halogenated hydrocarbons and the quantities of each transported to the sea might therefore be compared with the estimates of total biomass in the sea or with total organic productivity. The standing crop of plankton is in the order of 3×10^9 metric tons (D. Menzel, unpublished data) and the organic productivity is in the order of 2×10^{10} metric tons (Ryther, 1969).

The production of DDT in the U.S.A. is currently in the order of 50 000 metric tons (Chemical Economics Handbook, 1969) and global production is estimated to be no more than twice U.S. production (SCEP, Man's Impact on the Global Environment, 1970, p. 131). Production of the aldrin-toxaphene group of chlorinated hydrocarbon pesticides in the U.S.A. is also in the order of 50 000 metric tons (Chemical Economics Handbook, 1969). Exact data on the production of DDT and of the other chlorinated hydrocarbon insecticides in countries other than the U.S.A. are not readily available. The panel has not been able to obtain any estimate of the production of PCB, either on an individual country basis or on a global basis, in part because of legal systems that do not require manufacturers in the U.S.A. and Great Britain to release production figures upon request. Six hundred tons of unprocessed PCB and a small additional amount of PCB in manufactured goods are currently imported annually into Sweden; or approximately 100 grams per caput (Environmental Protection Board, Sweden). The populations of the industrialized countries of North America, Europe and Japan might therefore consume 50 000 tons per year. A knowledge of the global production figures of all synthetic chemicals that subsequently become waste products that enter the oceans would permit predictions of the potential impact of these pollutants upon marine food resources.

The amount of waste products in the form of chlorinated aliphatic hydrocarbons produced during manufacture of vinyl chlorides has been estimated to be 1-2% of the vinyl chloride produced. In northern Europe 75 000 tons of chlorinated aliphatic hydrocarbon wastes are produced annually by this process.

The DDT compounds have been shown to enter the sea in agricultural drainage waters, but it is unlikely that much more than 0.1% of annual production of DDT, or 100 metric tons, reach the ocean by surface runoff (Man's Impact on the Global Environment, 1970, p. 132). Up to 25% of annual production, however, may enter the sea in precipitation or in dry fallout (Ibid., p. 133), following drift, evaporation from lands, or following codistillation from water. PCB may also enter the sea in precipitation (Tarrant and Tatton, 1968) but to date no quantitative estimates of aerial fallout rates have been made. Incineration and codistillation of PCB from water may be sources of atmospheric PCB. PCB may also enter the sea in sewage (Ahling and Jensen, 1970), but we have not been able to assess the relative contributions of each source to the PCB now present in the sea. The source of some of the chlorinated aliphatic compounds now present in the sea (Jensen et al., 1970) is most likely dumping of factory wastes from tankers.

3.3 Monitoring systems

The panel was aware of the existence of only four pesticide monitoring schemes for the marine environment, only one of which is on an international scale. The three national schemes were operated by the U.S.A., U.K. and Sweden with an international programme organized under the Organization for Economic Cooperation and Development.

3.3.1 U.S.A.

A monitoring system of the estuarine areas has been in operation since 1965 and is based upon regular sampling and analysis of oysters, clams or mussels from a large number of stations in many American estuarine systems. The samples consisting of the flesh from 12 individuals, are homogenized, mixed with sodium sulphate in the field and transported back to the Gulf Breeze Laboratory of the National Marine Fisheries Service (NOAA, U.S.A.) (Butler, 1969).

3.3.2 U.K.

A monitoring system operated jointly by the Department of Agriculture and Fisheries of Scotland and the Ministry of Agriculture, Fisheries and Food has been in operation since 1969. Samples of cod, whiting, plaice, mackerel and herring are collected from 14 different fishing ports around the U.K. on a twice-yearly basis. Each sample consists of 10 individuals and an analysis is made of bulk homogenates of liver and muscle tissues for both PCBs and organo-chlorine pesticides. Details of the sampling, etc. have already been published (Holden and Portmann, 1969) and the results of the 1969 survey will be published in 1971.

3.3.3 Sweden

The Environmental Protection Board and the Swedish Museum of Natural History in Stockholm, together with the Institute of Marine Research, Lysekil, have cooperated in a monitoring scheme for Swedish coastal areas since 1969. Yellow eels and, when possible, pike, are collected from 52 areas along the coast once a year. Fifteen individuals are taken and of these five are analysed individually, together with an analysis of an homogenate of the remaining 10 fish. In addition, cod and herring are taken from 15 locations in Swedish coastal waters. Of these 15 places, 4 are sampled four times a year and the remainder twice. All samples are analysed for both PCBs and organo-chlorine pesticide residues.

3.3.4 OECD

The study group on the unintended occurrence of pesticides in the environment has organized a programme of monitoring of residue levels in aquatic wildlife. The species collected and analysed are pike, mussels and fish eating colonial birds (of which only eggs are analysed). Laboratories in about 13 different countries are now cooperating in the programme and samples are collected at set times of the year and an intercalibration of standards and exchange of samples aim to ensure that all results are comparable.

4. METHODS

4.1 Critique of existing methods

Methodology in the field of halogenated hydrocarbon analysis is rapidly evolving. It is likely that the several methods in use in 1970 will be modified over the next several years. Many techniques must be acquired by personal laboratory experience, and it is impossible to present in a short report all of the essential details. The following account must therefore be considered as an incomplete outline of current methodology and of the problems encountered in the analysis of environmental materials. A detailed discussion of analytical techniques is found in the Pesticide Analytical Manual (PAM) of the Food and Drug Administration of the United States. Portions of the manual are periodically revised as methodology is improved.

4.1.1 Preservation of specimens

Biological material can be preserved by wrapping in aluminium foil and freezing at -20°C until analysis. When freezing facilities are not available, preservation in 5-10% formalin is acceptable. It is absolutely essential that glassware and containers used to preserve specimens must be free of all substances that might produce interfering peaks on gas chromatographs (see paragraph 4.1.2). Many plastics contain PCB or other substances that may be extracted by solvents. These plastics must be avoided. Furthermore, it is prudent at this time to preserve material that might be examined in future years for pollutants undetected by current methods or that might serve as baseline material and controls for analysis of future pollutants. We recommend that all material of this nature be wrapped in aluminium foil and frozen. The aluminium foil, however, should first be checked for the presence of PCB or other potential contaminants.

4.1.2 Elimination of artifacts

Perhaps the most important part of the analysis of halogenated hydrocarbons is to ensure the absence of artifacts which may be acquired during the procedure. Several chlorinated hydrocarbons adsorb strongly to glass, and glass materials may therefore become contaminated by chlorinated hydrocarbons present as vapours in the laboratory. Many manufactured materials in the laboratory may contain PCB which may be leached by organic solvents. In addition, some plastics and many other materials contain substances that produce peaks in the electron capture detector. It is therefore essential that all solvents and materials used in the analysis be free of interfering substances. Glassware may be cleaned by initial rinses with acetone followed by immersion in hot water containing a strong detergent, additional rinses with water and drying in an oven. Intermediate rinses with acetone may be desirable. Solvents should be redistilled before use. Blank runs with the glassware and equivalent volumes of solvents used in the analyses should yield no peaks on gas chromatograms that might interfere with the determinations. Moreover, glassware used to analyse contaminated samples, such as sea birds, should be kept separate from glassware used in the analysis of other samples.

4.1.3 Sampling procedures

Marine organisms selected for monitoring should be chosen according to criteria that permit maximum amounts of scientific data to be obtained from each analysis. The collection period should be sufficiently long to reveal long-term trends. Relevant biological data include: site and depth of capture, date, weight of whole organism, percent lipid, breeding conditions, etc. The procedure adopted in Sweden for reporting monitoring data of this nature might be used (Jensen et al., 1969b).

When individual samples are combined to make composites, at least 10 specimens of each species should be taken at one time. In order to obtain meaningful and valid comparisons between series of samples taken at different times or locations, 15 analyses of individual organisms are usually an adequate compromise between too many samples and too few and sufficient to express the results in statistical terms. If fewer numbers of organisms are analysed and there is considerable variation in residue concentrations from individual to individual, the standard error of the mean may be large.

The results of such monitoring programmes will have significantly greater scientific value if an organo-chlorine pollutant budget is also drawn up for each site. Relevant data might include the amount of aerial fallout per unit surface area, amounts deposited in sediments per unit area and per unit time, and concentrations at points of time in the dominant components of the biomass, particulate material, and water. The relationships between the residues in water and the residues in the bivalves or fish analysed would thereby be determined. Also of value would be the determination of the relationships among residue concentrations, size, weight, age, lipid content, breeding condition, etc. for each species monitored. Food chain concentration effects, if any, might also be studied. Numbers acquired during routine monitoring would therefore have greater significance.

Bivalves and one or more species of fish would therefore be suitable species to monitor for chlorinated hydrocarbon at oceanic sites on a continuous on-going basis. The terminal carnivores such as seals, if material is available over long periods of time without the necessity of killing animals for the purpose of monitoring, might be considered suitable species to detect geographical variation in residue distribution (Holden, 1970). Several of the petrels and shearwaters have very wide distributions over the oceans and are, in addition, very abundant and are known to concentrate high amounts of residues. A population of the Wilson's petrel breeds in the Antarctic but ranges over the north and south Atlantic during the non-breeding season, another population is restricted to the south-east Pacific, a third is found in the area of the sea around Australia, while a fourth is restricted to the Indian Ocean. Other species range widely within areas of the sea such as the north Pacific, the south Atlantic, etc. Periodic collection of selected species or of their eggs at island breeding sites would therefore permit the following of accumulation trends over large areas of the sea.

4.1.4 Fat extraction

Since chlorinated hydrocarbons are associated with the lipid components of organisms, a preliminary step in the analysis consists of the extraction of lipid from the sample. The standard Torry method, using chloroform and methanol, is considered the most efficient fat extraction method; but other methods may yield equivalent amounts of chlorinated hydrocarbons.

A method currently in use in the laboratory of the Environmental Protection Board in Sweden yields lipid values equivalent to the Torry procedure. Ten grams of sample are homogenized in a funnel fitted with a fritted-glass filter with 25 ml of acetone and 10 ml of hexane. The liquid passes to a second funnel containing 75 ml of 0.9% sodium chloride solution. The sample is homogenized twice more with a 90:10

mixture of hexane and ethyl ether. The combined organic extracts are shaken with the sodium chloride solution in the second funnel, then re-extracted with 10 ml of hexane ether.

An alternative method consists of grinding the organism or portions thereof with anhydrous sodium sulphate in a Waring blender or with a mortar and pestle until a free-flowing powder is obtained. The powder is extracted in a soxhlet apparatus for six hours with a 2:1 mixture of hexane and acetone.

4.1.5 Lipid determination

It is important to determine the percentage of the extractable lipid in each sample, since lipid concentrations are believed to be closely related to physiological affects of these pollutants and in the case of aquatic organisms, to ambient water concentrations. Solvents in lipid samples should therefore be removed by evaporation techniques as described in the Pesticide Analytical Manual and dried by the addition of several millilitres of absolute ethyl alcohol. After the alcohol has evaporated, the sample is weighed.

4.1.6 Cleanup

Cleanup consists of the removal of lipids from the sample so that the remainder, containing the chlorinated hydrocarbons, may be injected into the gas chromatograph. A number of different methods are currently in use.

A column consisting of celite and fuming sulphuric acid permit the rapid cleanup of comparatively large amounts of lipid, but destroys dieldrin, endrin and similar insecticides (Stanley and LeFavoure, 1965).

Another cleanup method, which also destroys dieldrin and endrin but not the DDT compounds or PCB, consists of the addition of an aliquot (2-3 ml) of fat solution in hexane to two volumes of 6% fuming H_2SO_4, shaking, centrifugation and freezing in dry ice. The hexane solution can then be injected into the gas chromatograph, or separated into two or more fractions.

Holden and Marsden (1969) have described a method whereby fat is removed on an alumina column. This method is used in several laboratories and can be used for dieldrin and endrin analyses.

A cleanup method frequently recommended consists of the partition of extracts in hexane with acetonitrile or dimethylformanide. This method, which is suitable when dieldrin and endrin are also analysed, uses Florisil columns (Pesticide Analytical Manual). Recoveries of DDE and PCB, however, should be checked before the method is used on a routine basis.

4.1.7 Aliphatic chlorinated hydrocarbons

The preliminary study of these compounds in the sea (Jensen et al., 1970) describes briefly the methodology used to date.

4.1.8 Gas-liquid chromatography

Discussion of gas-liquid chromatography relating to many aspects of chlorinated hydrocarbon analysis are found in the papers by Burke (1965), Giuffrida et al. (1966) and Thompson et al. (1969a,b). Many different kinds of column materials are now available (Thompson et al., 1969a) for which particular chlorinated hydrocarbons will emerge at different times. Upon emerging from the column, materials such as the chlorinated hydrocarbons readily absorb electrons in the electron capture detector, producing a decrease in the standing current.

4.1.9 Quantification

Single components can be quantified by comparing peak heights with those of standards. PCB in samples, however, consist of mixtures of many different compounds frequently derived from different sources, and no quantification procedure has been universally accepted. We recommend, until better methods are devised, that the profile of the peaks identified as PCB in chromatograms be compared with those of standard PCB mixtures containing various percentages of chlorine by weight in order to determine which mixture the sample most closely resembles. The heights of one or more peaks can be compared with those produced by standards and an approximate concentration can be calculated. The methodology of PCB quantification is still in the development stage and refinements can be expected. A discussion of quantification procedure based upon peak heights is found in the Pesticide Analytical Manual.

4.1.10 Confirmation

Initial determination of chlorinated hydrocarbon compounds are made on the basis of retention times on one or more GIC columns. Conversion of a compound to a derivative with a different retention time provides confirmation. Thus, saponification (Hamence et al., 1965) converts p,p'-DDT, p,p'-DDD, and o,p'-DDT to their respective ethylene derivatives which have different retention times. P,p'-DDE can be converted by oxidation to p,p'-dichlorobenzophenone (DBP) (Westöö and Noren, 1970). Derivatives of dieldrin and endrin (Wiencke and Burke, 1969) may be prepared. DDE and other DDT compounds may also be removed from PCB by column chromatography (Armour and Burke, 1970). Initial identification of PCB is provided by the characteristic fingerprint of peaks in chromatograms. Confirmation of identity has been provided by mass spectrum analysis in several laboratories.

4.2 Design of inter-laboratory calibrations and formulation of primary and secondary standards

We do not recommend that a centralized laboratory be established at this time for the analysis of chlorinated hydrocarbons in samples collected in a global monitoring programme. It is in the best interest of developing countries to establish national laboratories whose activities might be integrated in a global programme with those of existing national programmes. It would be useful, however, to establish a centre from which primary standards might be distributed. These would include a series of standard PCBs with different percentages of chlorine composition. It would also be useful to distribute a standard column material for gas-liquid chromatography so that results from different laboratories might more easily be compared.

The establishment of fellowships would permit personnel to visit established laboratories to become familiar with techniques. It is important to establish a system whereby duplicate samples can be analysed in different laboratories. Failure to achieve equivalent results would thereby prompt a detailed examination of the techniques employed so that discrepancies might be corrected. A laboratory for this purpose might be established. Alternatively, several of the established laboratories might contract to analyse a certain number of sub-samples per year.

4.3 Automation

Advances are being made in the automation of certain steps of the analytical procedure. Automatic injection works well, but quantitative evaluation by computer techniques is not yet sufficiently formulated.

5. RESEARCH ACTIVITIES

The panel considered that there is a need for research in the following areas:

(a) Investigations into the metabolism of chlorinated hydrocarbons and particularly a search for polar derivatives not detected by present analytical procedures. Some of these compounds may have biological activity which might not be expressed until a critical concentration is reached. Areas of the sea where investigations might be made include Long Island Sound, the Baltic and the North Sea.

(b) Investigations into the possible presence of polychlorinated naphthalenes or their derivatives, and of fluorinated and brominated compounds in the marine environment.

(c) Investigations into the possible presence of chlorinated dibenzofurans in the marine environment. These are highly toxic by-products of PCB manufacture and may possibly be derived from PCB in the environment. Chlorinated dioxins which occur as impurities in certain chlorinated phenolic preparations are highly toxic, persistent, and fat soluble and should also be regarded as possible marine pollutants (U.S. Senate Hearings, 1970).

(d) Detailed investigations into the distribution of chlorinated hydrocarbons among the components of marine ecosystems, including water, particulate material, plankton, the dominant animals and plants of the biomass, sediments and surface films. The relationships between concentrations in fishes and other species and in water should be determined with a view to the possible indirect determination of concentrations of the chlorinated hydrocarbons in sea water.

(e) Determinations of the level of each major chlorinated hydrocarbon which would have deleterious effects on the marine environment as a whole, and continuing investigations of the effects on the individual components or combinations of the food web.

(f) Investigations into the metabolism, degradation rates and ecological effects of chlorinated hydrocarbon insecticide use in the tropical areas, and continuing investigations in other areas.

(g) Continuing investigations regarding the best way of quantifying PCB.

(h) Investigations into the fate of low-weight aliphatic chlorinated hydrocarbons used in the dry-cleaning and other industries in considerable amounts.

(i) Determination of the production figures on an individual country basis of each chlorinated hydrocarbon that subsequently becomes or is converted into a marine pollutant. These figures, together with the amounts imported and exported in each country, would permit the calculation of a budget for each pollutant and the determination of accumulation rates in the sea.

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7. LABORATORIES ENGAGED IN MONITORING AND/OR RESEARCH PROGRAMMES (Examples)

Canada	Canadian Wildlife Service 400 Laurier Avenue West Ottawa, Ontario	Mr. J.A. Keith
Germany (Federal Republic)	Bundesforschungsanstalt für Fischerei Institut für Küsten- und Binnenfischerei Palmaille 9 2 Hamburg 50	Dr. E. Huschenbeth
	Institut für Meeresforschung Am Handelshafen 12 285 Bremerhaven-G	Dr. W. Ernst
Netherlands	Institute of Veterinary Pharmacology and Toxicology University of Utrecht Utrecht	Dr. J.H. Koeman
Sweden	Naturvardsverkets Specialanalytiska Laboratorium Lantbrukshögskolan Uppsala 7	Prof. S. Jensen

U.K.	Ministry of Agriculture, Fisheries and Food Fisheries Laboratory Remembrance Avenue Burnham-on-Crouch, Essex	Dr. J.E. Portmann
	Department of Agriculture and Fisheries of Scotland Freshwater Fisheries Laboratory Faskally Pitlochry, Perthshire	Dr. A.V. Holden
	The Nature Conservancy Monks Wood Experimental Station Abbots Ripton, Huntingdonshire	Dr. N. Moore
	Laboratory of the Government Chemist Cornwall House Stamford Street London, S.E.1	Dr. D.C. Holmes
U.S.A.	Bodega Marine Laboratory Box 247 Bodega Bay, California 94923	Dr. C. Hand, Director Dr. R.W. Risebrough
	Gulf Breeze Laboratory Environmental Protection Agency 106 Matamoros Drive Gulf Breeze, Florida 32561	Dr. T.W. Duke Dr. P. Butler
	Bureau of Sport Fisheries and Wildlife Patuxent Wildlife Research Center Laurel, Maryland 20810	Dr. L. Stickel

Panel 2: PETROLEUM

M. Blumer (Chairman)
P.C. Blokker
E.B. Cowell
D.F. Duckworth

1. INTRODUCTION

1.1 Description of the pollutant

Hydrocarbons are ubiquitous in nature (Gerarde, 1962). In the marine environment hydrocarbons are derived from natural sources, e.g., from organisms (Blumer et al., 1964; Blumer and Thomas, 1965 a,b; Blumer et al., 1969, 1970 a,c; Clark and Blumer, 1967; Gelpi et al., 1968, 1970; Han et al., 1968, 1969; Youngblood et al., 1971) or from submarine seeps, or they are introduced through man's activity, e.g., in the form of pollution with fossil fuels. Hydrocarbons enter the sea at high and low concentration levels; at great dilution they are often not easily recognized visually, for instance if they are dissolved in the water (Blumer, 1970 c) or if they are present in dispersed form in the effluent from sewage outfalls.

The toxicity of various oils and oil products varies widely, depending on their composition, on environmental factors, on the biological state of the organisms at the time of the contamination. Different species and different life stages of organisms have been demonstrated to have different susceptibilities to pollution (Cowell, 1969; Crapp, 1970 a; Baker, 1970). Natural biogenic hydrocarbons may have well defined biological functions (Blumer, 1967; Youngblood et al., 1971). Therefore, methods for oil pollution research must be able to deal with the entire spectrum of oils and oil products at high and at low concentrations, as well as with the natural hydrocarbons in sediments and organisms. Further, for pollution research and for law enforcement we need to differentiate between biogenic hydrocarbons and oils from pollution or from submarine seeps. Also, we must be able to distinguish oils from different sources and oil products from different refining processes.

Petroleum hydrocarbons cover a wide range of molecular weights, from 16 (methane) to well above 20 000; structurally, they include compounds with straight and branched chains, olefins and saturated and aromatic ring compounds. Crude oils also contain hetero-compounds (with S,N,O, metals,etc.). The geochemical processes responsible for the formation of crude oil lead to the production of an immense number of individual hydrocarbons, including many isomers and members of different homologous series (Eglinton and Murphy, 1969). Also, a single molecule may contain straight or branched chain sub-units or saturated and aromatic rings. By convention, the presence in a hydrocarbon of a single aromatic, alicyclic or branched chain sub-unit, in that order of preference, is sufficient to classify it as an aromatic, alicyclic (cycloalkane, "naphthene") or branched chain hydrocarbon; if there are none of these sub-units, the hydrocarbon is a straight chain one.

Marked compositional differences exist between hydrocarbons from living organisms on one hand and oil from fossil fuels, derived from natural seeps or from pollution, on the other. Gas chromatography can detect these differences; sometimes preliminary separation is required. This provides the basis for the distinction between natural hydrocarbons and pollutants. Sometimes, hydrocarbons from one source can be detected in the presence of the other (Blumer et al., 1970 b,c.).

Compared to petroleum, biogenic hydrocarbons have a rather narrow molecular weight range; a few components or even a single one may far exceed in concentration all other components. As far as is known, straight chain compounds, saturated and olefinic, predominate; branched hydrocarbons, especially isoprenoid alkanes and alkenes, are formed by many marine organisms but they cover only a narrow molecular weight range. Cycloalkanes and aromatics are not as generally abundant in organisms as in petroleum. Crude oil covers a very wide molecular weight range, and numerous homologous series are represented. Usually, adjacent members of these series vary little in concentration. Olefins, which are abundant in organisms, do not occur in crude oils but they can be present in refinery products.

Alicyclic and aromatic hydrocarbons are abundant in petroleum. Substituted ring compounds are more abundant than their parents. The number of substituted derivatives and the complexity of the substitution is greater than in the cyclic hydrocarbon fraction of organisms. Heavy asphaltic compounds are associated with the majority of crude oils, though not necessarily with refining products; they do not occur naturally in organisms.

The hydrocarbon content of many marine organisms has been studied; but so far most specimens have been obtained from the coastal waters of the northeastern U.S.A. and from the North Atlantic. The same general hydrocarbon type composition may also be found in organisms from other areas of the world oceans, though the specific composition varies greatly, often from species to species. Studies of this kind are urgently needed in other oceanic regions in order to establish the present level of natural and fossil fuel derived hydrocarbons on a world wide scale.

Different oils and oil products exhibit a great variety of composition in spite of their overall similarities. Each oil is made up of many thousands or ten thousands of individual compounds. The variety of geochemical and refining processes which each oil underwent, has imprinted on it characteristic compositional and structural features. Thus, analytical techniques, capable of high resolution, can be used to distinguish crude oils from different sources. The correlation between different crude oils and between oils and their source sediments is of great value in petroleum exploration. Therefore, major efforts have been devoted by oil research laboratories to the development of techniques for crude oil characterization and correlation (Philippi, 1965; Boulet and Guichard-Loudet, 1968; Oudin, 1970). The application of such techniques should be of great value to oil pollution research and law enforcement.

Crude oil and oil products spilled in nature are altered by evaporation, by dissolution, by bacterial and by chemical attack. Not all hydrocarbons are affected at the same rate. Environmental exposure ("ageing, weathering") affects both the contamination level and the relative composition of the pollutant (Cowell, 1969; Baker, 1970; Blumer et al., 1970 c).

In spite of the complex processes occurring during weathering, many compositional parameters are relatively stable and are not obliterated until an advanced stage of degradation has been reached (Blumer et al., 1970 c; Duckworth, 1970). These stable parameters may aid in the identification of an oil pollutant and in the correlation with its source for many weeks if not months after the spill.

1.2 Concentration of petroleum pollutants in the environment

Petroleum pollutants in the ocean may occur at any concentration between bulk oil and oil at very low concentration level, such as

(a) Floating material
(b) Emulsions dispersed in sea water
(c) Dissolved in water
(d) Adsorbed on sediments
(e) In marine organisms

Little information is available on the extent of pollution in the different marine ecosystems. In the past, insufficient interest, together with analytical difficulties, have been responsible for slow progress in the accumulation of measurements of the levels of oil pollution in the sea. More sensitive and selective analytical techniques are available now and we can measure petroleum hydrocarbons at levels corresponding to the natural hydrocarbon background.

Such techniques are now being applied to the analysis of polluted sediments and of polluted shellfish (Blumer et al., 1970 b,c) and fish specimens (Sidhu et al., 1970). In a study of the long term effects of a distillate fuel oil spill, it has been shown that toxicity in polluted sediments can be demonstrated wherever oil can be detected by gas chromatography (Blumer et al., 1970 c).

The uptake of oil and other pollutants into marine organisms and the resulting "tainting" has long been described (Simpson, 1968; Crapp, 1970 a). However, objective measurements of the oil pollution levels of fisheries products are possible now and should be of value to public health authorities.

1.3 The use of petroleum and the extent of marine pollution

Oil pollution is the almost inevitable consequence of the dependence of a growing population on an increasingly oil-based technology. The widespread production and transportation of oil and its use as fuel, lubricant and chemical raw product leads to losses which are wide, but not evenly spread. Production and transportation estimates for 1970 and 1980 are given in Table I. Estimates for the amount of oil spilled, deliberately or accidentally, into the ocean vary and suggest an input between 1 and 10 million tons/year (Hunt and Blumer, 1970; Blumer, 1970 a,b).

Oil transport is not evenly distributed over the ocean surface; it is more heavily concentrated along the continental shelves in coastal areas and in regions of upwelling water (Figure 1). These are also areas of great biomass productivity (Ryther, 1969); damage from oil pollution may therefore be greater than if the oil influx were evenly spread over the ocean.

TABLE I

World Petroleum Production and Transportation (Hunt and Blumer, 1970)
(in million metric tons)

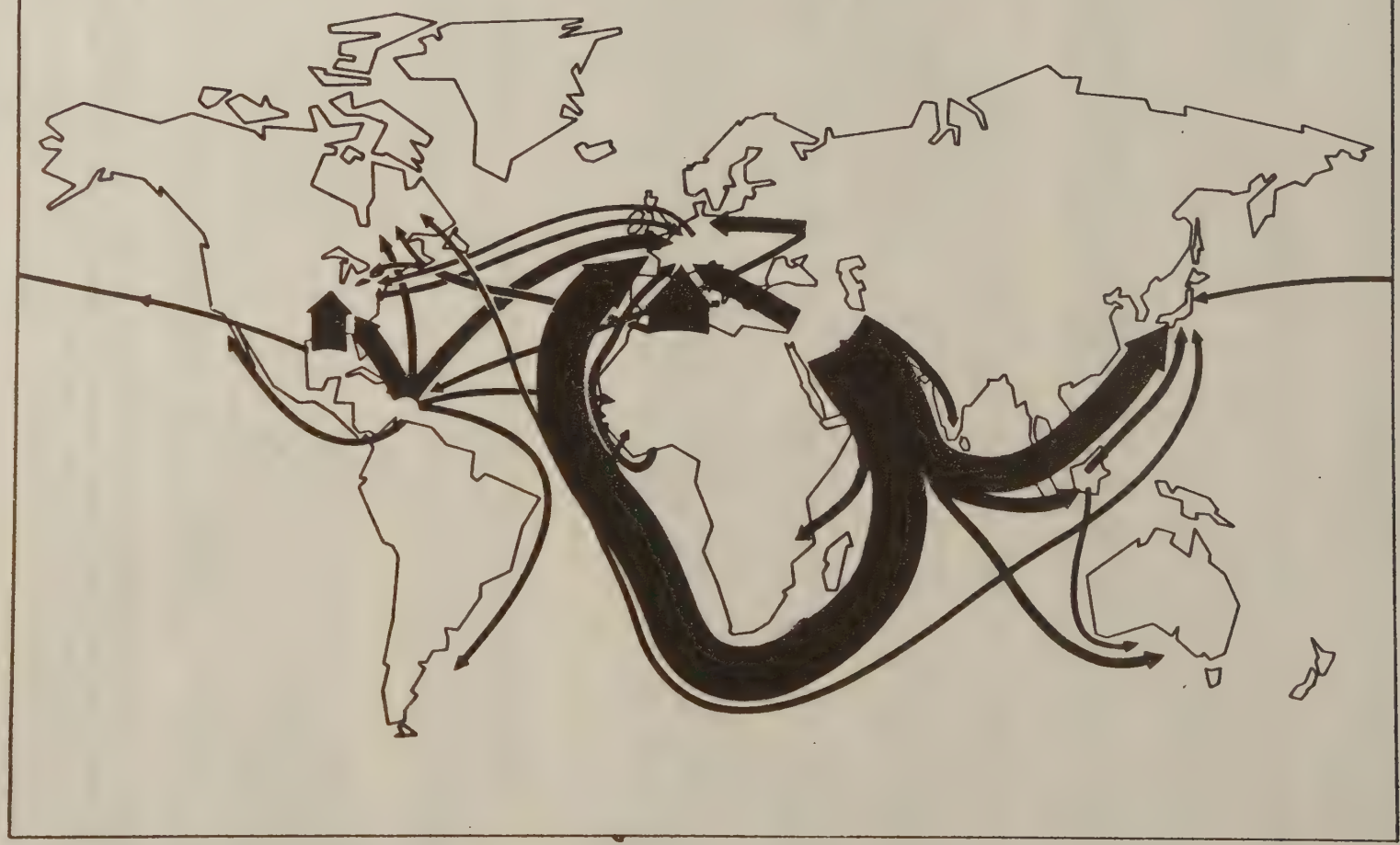
	1967	1970	1980 (estim.)
Production, total	1 850	2 200	4 000
Production, offshore	260	440	1 300
Tanker cargoes, total	650	1 500	2 900
Petroleum reserves	57 000	75 000	?*

* Ultimate world offshore potential to 350 m water depth estimate at 220 000 x 10^6 metric tons.

Present figures are not sufficiently accurate to assess the degree of pollution of different oceanic regions by different crude oils and oil products. Much better and more detailed surveys, especially in the most productive regions of the oceans, are urgently needed, if we are to estimate the effect of oil pollution on marine ecosystems and on fisheries resources.

Figure 1:

MAIN OIL MOVEMENTS BY SEA 1968



(British Petroleum, 1969)

Different oils and oil products vary in their toxicity (Ottway, 1970) and in the mode by which they interfere with marine life processes. Generally, distillates up to and including gas oils are more severely toxic on a short time scale than the other components of crude oil. These, on the other hand, may contain more slow acting compounds, like the polycyclic aromatic hydrocarbons, and compounds that may interfere with some of the vital life processes of marine organisms (Blumer, 1970 b).

The terminology of oil refining products differs between countries, making comparisons of their composition difficult. 1/ However, the descriptive terms of the refining industry (e.g., fuel oil, bunker oil) are not chemical descriptions; the composition of such products can vary widely, depending on their source and refining history. Often, such products are blends derived from several processes within the refinery.

1.4 Monitoring systems

Monitoring of oil should aim not only at the detection of spills but also at ascertaining long-term changes in marine systems and in the degree of pollution of the ocean. Because insufficient knowledge exists on the long-term effects of pollution, monitoring of oil in water, organisms and sediments is urgently required.

A number of techniques that could be used for the monitoring of hydrocarbons, especially on the sea surface, exist. None of the physical techniques are specific for individual hydrocarbons. Therefore, and because of the limited concentration range which can be covered at present, these techniques are of little value in studying the long-term fate of oil in the environment. However, monitoring at relatively high concentrations, especially after large spills, is possible.

Monitoring techniques are based, for instance, on measurements of optical densities at various wavelengths, electrical conductivity, fluorescence, etc. More specific chemical surveys are possible by gas chromatography. This is being used on sea-going vessels for the purpose of petroleum exploration (Jeffrey and Zarrella, 1970). Applications have been limited to low boiling hydrocarbons, up to butane or pentane, mainly by the sampling technique which involves stripping the most volatile components from a water stream. Thus, such a system might detect a fresh slick containing low boiling hydrocarbons; however, the more usual aged slick, which has lost the low boiling components would not be detected by the existing instruments.

These different techniques can complement each other, physical sensors may provide information on volume and area of the slick, while gas chromatography may help in the identification of the material that has been spilled.

Remote sensing systems, using, for instance, thermal infra-red imaging by overflights and using densitometric colour enhancement of the infra-red images and automatic digital planimetry of the areas of specified image densities (Estes and Golomb, 1970; Noble, 1970; Swaby, 1970) can estimate volumes and flow rates and changes in area and extent of the spill. The technical sophistication makes this a specialist's technique; also such methods do not - at this time - distinguish between natural slicks from marine lipids and fossil fuels. Differences in the absorption spectra of natural lipids and fossil fuels might be utilized for the distinction between these types of surface films. Attention should be devoted during the further development of remote sensing to the need to differentiate between surface films of different origin.

Equipment for remote infra-red sensing is already installed in commercial aircraft and can be flown to problem areas on short notice.

1/ Some assistance is given by: Standard Specifications for Fuel Oils (ASTM D396-69), or by: A Glossary of Petroleum Terms (Institute of Petroleum, 1967).

2. EXISTING METHODS

2.1 Hydrocarbon analysis of water, sediments and organisms

The field of hydrocarbon analysis is covered by a vast literature which cannot be fully reviewed here. Comprehensive and up-to-date reviews are available, for instance, in Analytical Chemistry. (Fundamental and applied progress is reviewed in alternating years: see the most current reviews in the April 1970 and 1971 issues). The separation and identification of petroleum constituents have been discussed by Powell and Whitehead (1971) (Figures 2 and 3).

For petroleum pollutant analysis it is not possible to provide specific methods of detection, etc. as can be done for pollutants which consist of a single compound or group of compounds. This is because any technique has to deal with the immense number of individual hydrocarbons that compose crude petroleum and its primary products. The matter is further complicated by the extremely wide range of concentrations to be considered and the different purposes for which the analyses are required. Thus a somewhat generalized analytical scheme has had to be given. Methods possessing sufficient sensitivity and selectivity will be emphasized here. Ideally, methods for pollution research should be able to cover the whole concentration range from bulk oil to oil traces in sediments and organisms.

The majority of these techniques are sufficiently sensitive and selective for the investigation of the behaviour of petroleum materials in the marine environment. They are not aimed at rapid routine surveys but at detailed examination of selected materials. Simpler and more rapid methods will often be entirely adequate to establish the identity of a gross spill with its source.

2.1.1. Correlation of spilled oil and its source

Two different principles have been proposed for the correlation between spilled oil and its sources. Active tagging involves the incorporation into oil during transport of certain compounds (e.g., dyes, fluorescent materials, trace metals, radioactive isotopes, etc.) that can be recognized readily in any spill. The range of potential tags is too wide to be covered here, also, implicitly, a tag will be selected specifically for the ease of its analytical detection, among other criteria. It is doubtful whether active tagging will be applied universally on a world wide basis since it depends on many factors: general cooperation, development of a suitable system and numerous uncertainties, such as a sufficiently wide range of tags, and the stability of the tag, which should persist during transport but not enter the refined products. Active tagging may not be useful for the monitoring of pollution on a world wide scale and it will be of little help in the study of the fate of oil in the environment, especially in the biosphere.

Passive tagging utilizes the wide natural compositional differences that can occur between crude oils from different wells, fields, storage tanks and between oils that have been subjected to different refining processes. In their composition, oil and oil products are enormously complex and almost infinitely variable. It is possible to find many compositional parameters that are characteristic for a given oil and that resist the effect of weathering for a sufficient time for use in law enforcement (Jeltes and Veldink, 1967; Brunnock et al., 1968; Ramsdale and Wilkinson, 1968; Blumer et al., 1970 c).

A highly selective analytical technique can produce from each oil sample a very characteristic fingerprint. Such methods are used routinely and successfully on very small samples for geochemical crude oil correlation (Philippi, 1965; Boulet and Guichard-Loudet 1968; Oudin, 1970). Pollution studies have only now begun to use such techniques and the full potential of these high resolution analytical methods has not yet been realized in this field.

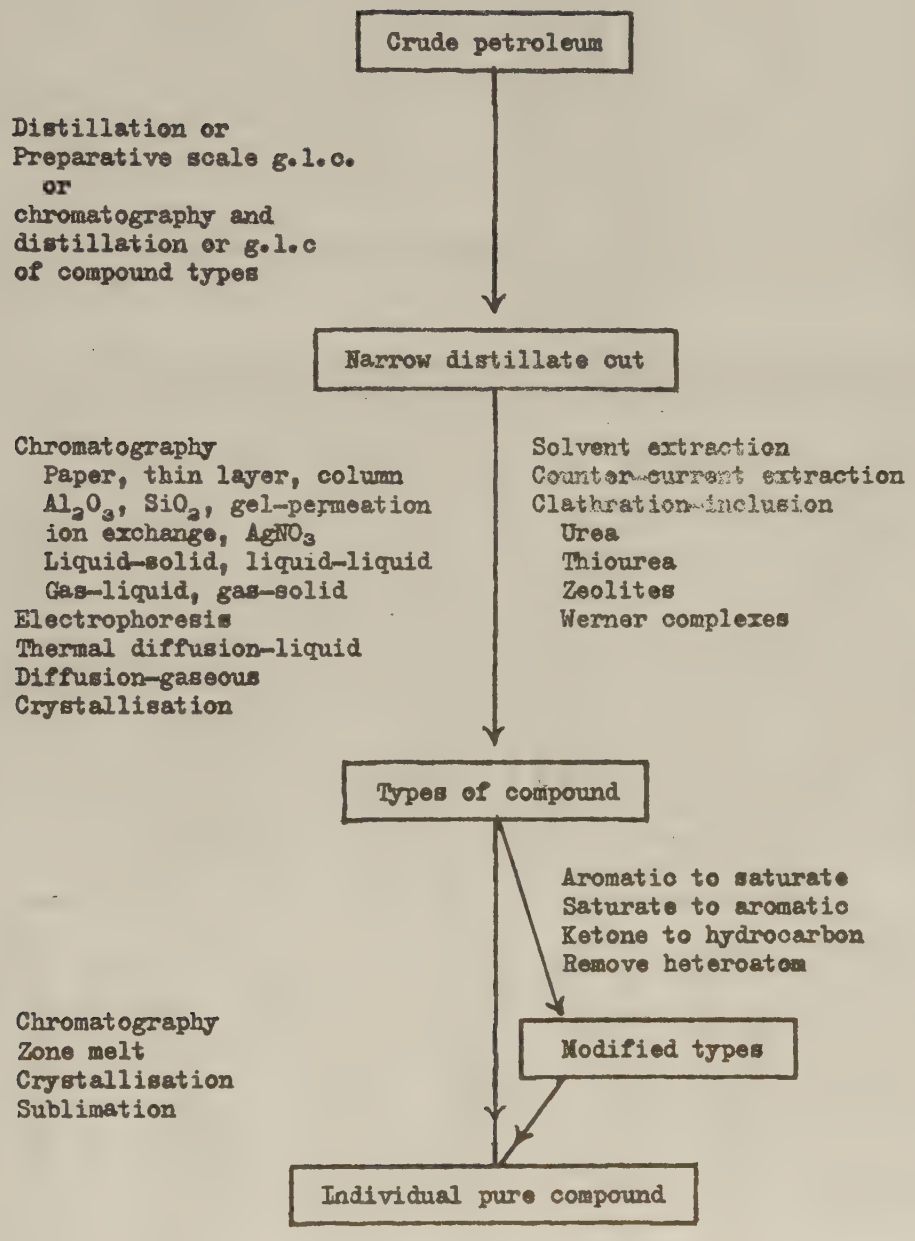


Figure 2: Separation of petroleum constituents

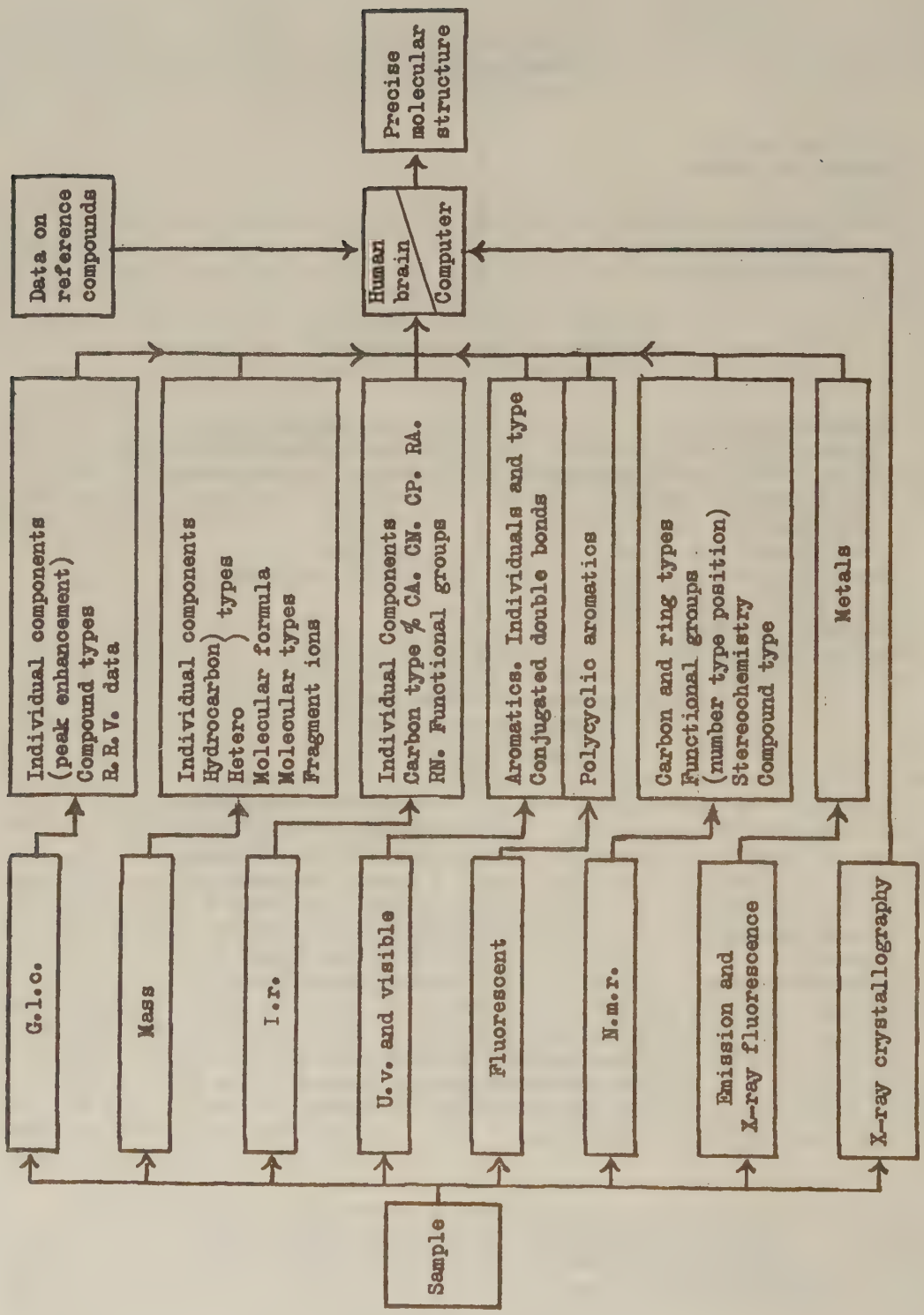


Figure 3: Analysis of petroleum constituents

2.1.2. The choice of analytical technique

Analytical techniques for the determination of compositional changes undergone by hydrocarbon pollutants should be compared in terms of their cost effectiveness. (This corresponds essentially to the ratio of useful data produced to the labour expended, since instrumentation costs in the long run become negligible.) In these terms, subjective, observational techniques (physiological evaluation of smell and taste, observation of fluorescence of bulk extracts or of thin layer chromatograms) are rarely highly productive of useful information. Measurements of single parameters on bulk oil samples similarly offer little return for the analytical effort (C,N,S,O,V,Ni, etc., content, wax content, asphaltene content, etc.). As Cole (1968) has pointed out, physical properties (density, congealing point, viscosity, aniline point, etc.) are often so closely linked to the boiling range and hydrocarbon type content of an oil that the determination of these data adds nothing to that available from GC and IR analysis. The use of these physical and single analytical measurements is therefore not recommended except in special cases.

Spectral techniques (UV, IR, nmr, MS, spectrofluorimetry) applied to whole oils (Kawahara, 1969; Mattson et al., 1970) offer a higher return of information; this is especially true for mass spectrometry which can be useful even if applied to unresolved whole oil samples. However, by their nature and because of the great complexity of oil and oil products, the remaining spectral techniques rarely observe properties of individual compounds. Rather, they are concerned with an "average" molecule and they measure the presence of certain functional groups within all the compounds present in the oil. Even with this limitation, infra-red analysis in conjunction with highly selective gas chromatographic separations has been used successfully to identify pollutants (Cole, 1968; Kreider, 1970). On the whole, however, these techniques produce better and more abundant data, if they are applied not to the bulk oil samples but to fractions obtained by a highly selective fractionation technique. Thus, infra-red analysis after thin layer chromatography provides much more information on the saturated and olefinic hydrocarbons in a sample than IR analysis of the bulk sample. Similarly, IR or UV spectroscopy applied to polycyclic aromatic hydrocarbons collected from a gas chromatographic column may at low and intermediate molecular weights conclusively identify ring type and type and degree of substitution; this would be impossible to achieve by the analysis of a bulk sample. The same philosophy applies to the extremely powerful combination of gas chromatography with mass spectrometry.

Highly selective analytical techniques provide the greatest data return for the effort expended. Ideally, these techniques, especially high resolution gas chromatography and, to a lesser degree, gel permeation chromatography, are capable of defining some of the immense complexity of the oil samples. If necessary these techniques can be combined with spectral techniques that may give exact structural assignments on individual compounds isolated from the oil. Gas chromatography and gel permeation chromatography complement each other, the former is most useful in the approximate $C_1 - C_{40}$ range, while the usefulness of GPC extends from roughly C_{10} into the high molecular weight range. These techniques are also sensitive and permit analysis of the small samples obtainable from polluted marine organisms and sediments.

2.2. Isolation of the hydrocarbons

The further discussion will emphasize the isolation and separation of pollution samples to make them available in a form that is readily subjected to gas chromatography. In spite of the initial investment and of the care needed in equipment maintenance, gas chromatography is so far superior to other techniques in terms of sensitivity, selectivity and universal applicability that newly established pollution laboratories should be urged to establish first a GC capability. At a later point this might be complemented by spectral analytical tools, including mass spectrometry.

Hydrocarbon pollutants may be obtained for analysis as bulk samples or as oils that are finely dispersed, adsorbed or dissolved. In the case of bulk oil samples little or no preliminary concentration or separation is needed. The sample may be dissolved for injection into the gas chromatograph (CS_2 has the advantage both of being a good solvent and of producing little response in the hydrogen flame detector). Water may be removed by centrifugation of the bulk oil or of its solution. The sample may also be introduced into the chromatograph without the addition of solvent (see below).

In the case of finely dispersed, adsorbed or dissolved oil a more complex extraction (Blumer, 1970 c, Blumer et al., 1970 b,c) and possibly a separation are necessary.

2.2.1. The pollutant predominates over the indigenous lipids

This situation is encountered in polluted sediments. In preparation for the extraction the wet sample may be dried, unless loss of low boiling hydrocarbons would result. Extraction may be carried out by the slow Soxhlet extraction technique or by the more rapid ultrasonic extraction method (McIver, 1962). Methanol-benzene azeotrope serves as a useful solvent, both for dry and wet sediment samples. In the latter case an extract consisting of two phases is obtained. These are separated, the aqueous phase is washed with an organic solvent (e.g., pentane) and the combined organic phases are dried and concentrated by evaporation, preferably on a rotating evaporator at a moderate or low temperature. The extract may be gas chromatographed directly or it may be subjected to removal of sulphur (Blumer, 1957) and chromatographic separation on adsorbent columns or thin layers.

The possibility of the formation of artifacts in ultrasonically aided extraction should be kept in mind. It has been shown that wet halogenated solvents may be decomposed by ultrasonic irradiation, free chlorine is produced instantaneously (Spurlock and Reifsneider, 1969; Weissler, 1962). A systematic study of the relative reliability of this widely used technique appears long overdue.

2.2.2. The pollutant is present together with natural lipids

Hydrocarbon pollutants in plants and animals are almost always accompanied by natural lipids which interfere with the direct gas chromatographic analysis (in some instances distillative separation in the GC inlet is possible, see 2.3.1 below). If only the saturated hydrocarbon fraction is to be analysed or if the oil pollutant is of suitable boiling range (boiling below 350°C), column chromatography may be sufficient for the isolation of the hydrocarbons of interest. Silica gel is used in this case because of the good resolution between saturated and aromatic hydrocarbons; the addition of a short alumina bed on top of the silica gel bed aids in the retention of the more polar higher molecular weight materials for which silica gel has only a limited capacity (Blumer et al., 1970 c). Both absorbents should be partially deactivated by the addition of water to prevent the formation of artifacts (Johnstone and Quan, 1963; Blumer et al., 1970 c). These techniques have been used for the isolation of natural saturated and olefinic hydrocarbons in plants and animals and for the analysis of fuel oil spilled and taken up by sediments and organisms.

In the case of oils of high boiling range, extending above C_{25}, and in those instances where all aromatic hydrocarbons should be recovered, a more extensive separation is needed before GC can be applied. Unfortunately, the multi-ring aromatic hydrocarbons elute from silica gel and alumina together with the triglyceride lipids. The separation of the hydrocarbons from the lipids can be achieved either by extensive and time-consuming repetitive thin layer chromatography or by saponification of the lipids, especially by the elegant and rapid hydrolysis in homogeneous solution (methanol-sodium hydroxide) according to Metcalfe et al. (1966). After addition of a small amount of water, the methanol phase can be extracted by pentane. The extract contains all hydrocarbons and only minor quantities

of fatty materials (e.g., alcohols) which may be removed by thin layer or column chromatography, if necessary.

Other separating techniques may be used on occasion. Thus, the normal paraffins can be selectively removed by 5△molecular sieve adsorption on a macro (Brunnock, 1966) or micro scale (Mortimer and Luke, 1967); urea clathration has been used on microgram samples with excellent results though it is less specific than molecular sieve adsorption (Douglas et al., 1971). Distillation of microsamples (Javes et al., 1955) has been superseded largely by gas chromotography, but a relatively efficient molecular still, requiring only milligram samples, may be used occasionally, especially since it can handle samples boiling at the upper range of GC usefulness (Blumer 1962).

2.3 Gas chromatography

Numerous textbooks and scientific papers cover the field of gas chromatography, including the analysis of hydrocarbon samples. Therefore only a few special aspects, directly relating to pollution, are covered here.

2.3.1. Sample introduction

Samples may be introduced as conventional, in solution, by on column injection or by vaporization in a heated injection block. Carbon disulphide is a suitable solvent. Some special introduction techniques are applicable to the pollution field. Thus, the British Institute of Petroleum Standardization Committee has described a modified inlet system that accepts a solvent free oil sample in a glass tube. The tube is inserted via two ball valves into the heated injector (Anon., 1970). A similar but simpler technique involves the rapid insertion into the injector of the oil contained inside a short piece of glass tubing. The injector is immediately closed by septum and nut. The tube is left in the injector at a temperature and for a time that assures evaporation of the hydrocarbons but minimizes thermal decomposition of the residue. The front end of the column is cooled with air or dry ice. Later, the glass tube containing the residue is withdrawn and the temperature programme is started. In this way the injection port remains clean. The technique is highly tolerant of the presence of high boiling materials, e.g., asphaltenes, lipids (Blumer, unpublished).

2.3.2. Column selection

For hydrocarbon analysis one chooses routinely non-polar gas chromatographic substrates (e.g., silicone rubbers, Apiezon L). In the case of the analysis for more polar hydrocarbons, e.g., olefins, aromatics, more information about structural properties can be obtained by performing separate separations on two different substrates, one non-polar, the other highly polar (e.g., FFAP, Varian Aerograph) and by using the retention index concept (Kovats, 1958; Wehrli and Kovats, 1959) in the evaluation of the data.

Standards for the selection of column packings and column lengths have been proposed (Anon., 1970). It has been suggested that the columns should be of sufficient efficiency to resolve partly the pairs pristane-n-heptadecane and phytane-n-octadecane (Kreider, 1970). However, in some special cases more rapid analysis on less efficient columns is possible (analysis of isolated normal paraffins), while in other cases more efficient columns yield a better fingerprint characterization of the oil. For intercomparison between laboratories the substrate used and the plate efficiency of the columns should be specified.

Capillary or packed columns of various internal diameters may be used; often packed 1/16 inch o.d. columns or 1/8 inch o.d. narrow bore columns give a good compromise between the larger packed and the capillary columns. Flow rates should be adjusted for optimum plate efficiency.

2.3.3. Sample recovery

Various instruments and techniques have been described for preparative gas chromotography or for the trapping of materials in column effluents. Large preparative gas chromatographs often suffer from inadequate plate efficiency, poor recovery of small samples; thermal decomposition of small samples, especially of olefins, on the necessarily large columns is common. Sufficient sample for further analysis can be recovered from efficient analytical columns. Thus, many studies on natural hydrocarbons in organisms have used the efficient trapping of samples from a modified flame tip in a melting point capillary, whose interior has been roughed with carborundum powder in order to provide a larger surface area (Blumer et al., 1969). Microgram samples can be recovered with high yields. Thus, sufficient sample for further spectral, chemical and chromatographic analysis can be recovered.

2.4 Gel permeation chromatography

For investigation of the major percentage of crude oil components gas chromatography is superior to gel permeation chromatography (GPC); however, the latter has a greater potential in the high molecular weight range where GC is becoming impractical because of limitations in the volatility of the samples.

Several papers deal with the separation of crude oils, crude oil fractions, asphaltenes and oil derived porphyrin pigments by gel permeation chromatography (Blumer and Snyder, 1967; Blumer and Rudrum, 1970; additional references see Done and Reid, 1970). The potential of this technique specifically for oil pollution research has been discussed (Done and Reid, 1970).

Gel permeation chromatography (GPC) is as easily automated as GC and is capable of comparable separating efficiency. Therefore, GPC is particularly attractive for the analysis of high boiling oils such as bunker oils, distillation residues, heavy asphaltic oil and tars and oils that have undergone very severe weathering.

At the present time, the non-ideal behaviour of many GPC substrates (especially Sephadex LH-20) limits their applicability, since the more polar fractions of heavy oils are irreversibly adsorbed or at least strongly retained. Thus, at the present state of the art, these materials have to be removed, e.g., by asphaltene precitipation or by column chromatography. Except for this limitation, excellent molecular weight separations of heavy oils and oil fractions are possible (Nyström and Sjövall, 1965).

2.5 Observations on existing methods

2.5.1. Spectral analysis of GC eluates

GC on small packed columns provides sufficient samples for further spectral analysis. The simplest though not cheapest approach uses a direct interface between GC column and mass spectrometer or IR spectrophotometer. Column effluents can also be trapped as described above (2.3.3) and they can then be analysed by spectroscopic instruments. By using a beam condenser and a mask of approximately 4 mm^2 infra-red spectra of excellent quality can be obtained on samples ranging from 1-10 micrograms. Measurements can be carried out on solutions in microcells, on liquids between salt plates or on solids in micro KBr pellets. Spectra of smaller samples may be obtained through the use of time averaging of repetitive scans, or possibly by the use of Fourier transform analysis.

In general, smaller infra-red instruments perform well, since their weaker sources lead to less heating and lower sample loss by evaporation than the more powerful sources of larger instruments. Similarly, UV- spectrophotometers are preferred that expose the sample to the dispersed radiation rather than to the full intensity of the undispersed beam.

2.5.2. Contamination problems

Sample contamination during sampling and analysis is unavoidable. For meaningful analyses the contamination level has to be reduced well below the concentration of the pollutant which is to be analysed. With bulk oil samples this is not difficult; however, it becomes increasingly difficult as one approaches the natural hydrocarbon background level.

Contamination from lubricants, silicones, plasticizers (phthalate and sebacate esters), skin lipids, polluted air and even cleaned laboratory air (Blumer, 1965) is common. Fossil hydrocarbons occur in common laboratory solvents and are difficult to remove by distillation (Blumer and Snyder, 1965).

Further, hydrocarbon artifacts may be formed during the analytical sample work-up. Thus, phytadienes are formed on gas or liquid chromatographic columns from phytol by dehydration (Johnstone and Quan, 1963). Phytol and other sensitive alcohols are always present in biological samples. Therefore, adsorbent columns should be deactivated with water, even if this causes some loss of separating efficiency, and samples containing such sensitive compounds should not be subjected to gas chromatography without preliminary chromatographic removal of the sensitive polar materials.

2.6 Interlaboratory calibration; primary and secondary standards

Hydrocarbons are encountered in nature in great structural complexity and within a very great concentration range. It may be difficult to formulate primary and secondary standards suitable for analyses representative of this wide compositional range; standards typical for polluted biological samples may not be readily preserved.

A central agency might provide:

(a) a limited range of hydrocarbon standards (pure single compounds, artificial blends of stable hydrocarbons) suitable for calibration of methods requiring high precision and repeatability,

(b) a wide range of crude oils and refinery products covering the types of materials that are likely to be found in the seas.

In addition, libraries of gas chromatograms representative of a wide range of crude oils and oil products, carried out under standardized analytical conditions, and possibly at different column efficiencies (low, medium and high resolution) should be made available.

2.7 Automation of techniques

The great structural variability and the wide concentration range of hydrocarbons in nature make the design of automatic monitoring techniques and equipment difficult. Individual steps within the analysis scheme are amenable to automation and may in certain cases, e.g., in the analysis of bulk oils, permit almost fully automated analyses. Automated gas chromatography with repetitive sample injection, analysis, recording, integration and data output in digital or analogue form is practicable.

In those cases, where the fate of the hydrocarbons in nature is being studied, additional sample concentration is necessary before the analysis. This and the final data evaluation are neither easily automated nor independent of the judgement of the analytical chemist.

3. IDENTIFICATION OF RESEARCH ACTIVITIES

3.1 Methods for obtaining oil samples, especially from surface films

Methods have been developed for the recovery of surface oil films (Garrett, 1962); however, satisfactory collection of slicks and of oil contaminated water from any depth and at all sea states is still difficult. Further development in this area is needed; consideration should be given to the possible contamination of the samples on board the vessel.

3.2 Hydrocarbon analysis of biological samples from the open ocean

It is possible that routine sampling of plankton, nekton and benthos and analysis of their lipids for hydrocarbons could provide a basis for monitoring the levels of oil in the oceans. The techniques for collecting samples with continuous plankton recorders (Hardy, 1939) on ocean going vessels are well established (Glover et al., 1970) and need no further technological advances, besides those necessary to assure freedom from contamination, to be set up on a global scale. Problems would arise due to considerable seasonal and cyclical changes in plankton populations. A great deal of basic research is needed to establish the degree of uniformity or of selectivity of hydrocarbon transfer from the water into organisms and through the marine food web. The problems of pollution must not be considered in isolation from those of ecology as a whole (Lewis, 1970). Research is needed at all points indicated by arrows in Fig. 4. Both laboratory and theoretical studies have indicated the parameters that should be measured but little basic work has been done. These difficulties could be overcome if sufficient funds for the necessary basic research were made available.

3.3 Biological monitoring of the effects of oil on the intertidal zone

The value of biological monitoring is well established. From comparison of the various methods we recommend that a rapid method for examining a large number of sites produces useful data more rapidly than very detailed counts in a limited number of areas (Crapp, 1970 c). All monitoring of the effects of oil via the monitoring of organisms should be carried out against detailed background study, both chemical and biological.

3.4 Detection and monitoring

The methods described in this panel report should not be considered final standard methods; they are in part research techniques which are apt to be changed. Further development of the analytical techniques is necessary, especially for samples lying outside the range of those dealt with so far.

3.5 Environmental fate of the oil

We are still ignorant about the fate of oil in many marine ecosystems and about the products of bacterial oil degradation. Compositional and toxicological studies of the hydrocarbons and their environmental degradation products are needed. Studies are also required to define the mechanisms and rates of dissipation of hydrocarbons from floating or dispersed oil by such processes as evaporation, dissolution, partitioning and bacterial degradation.

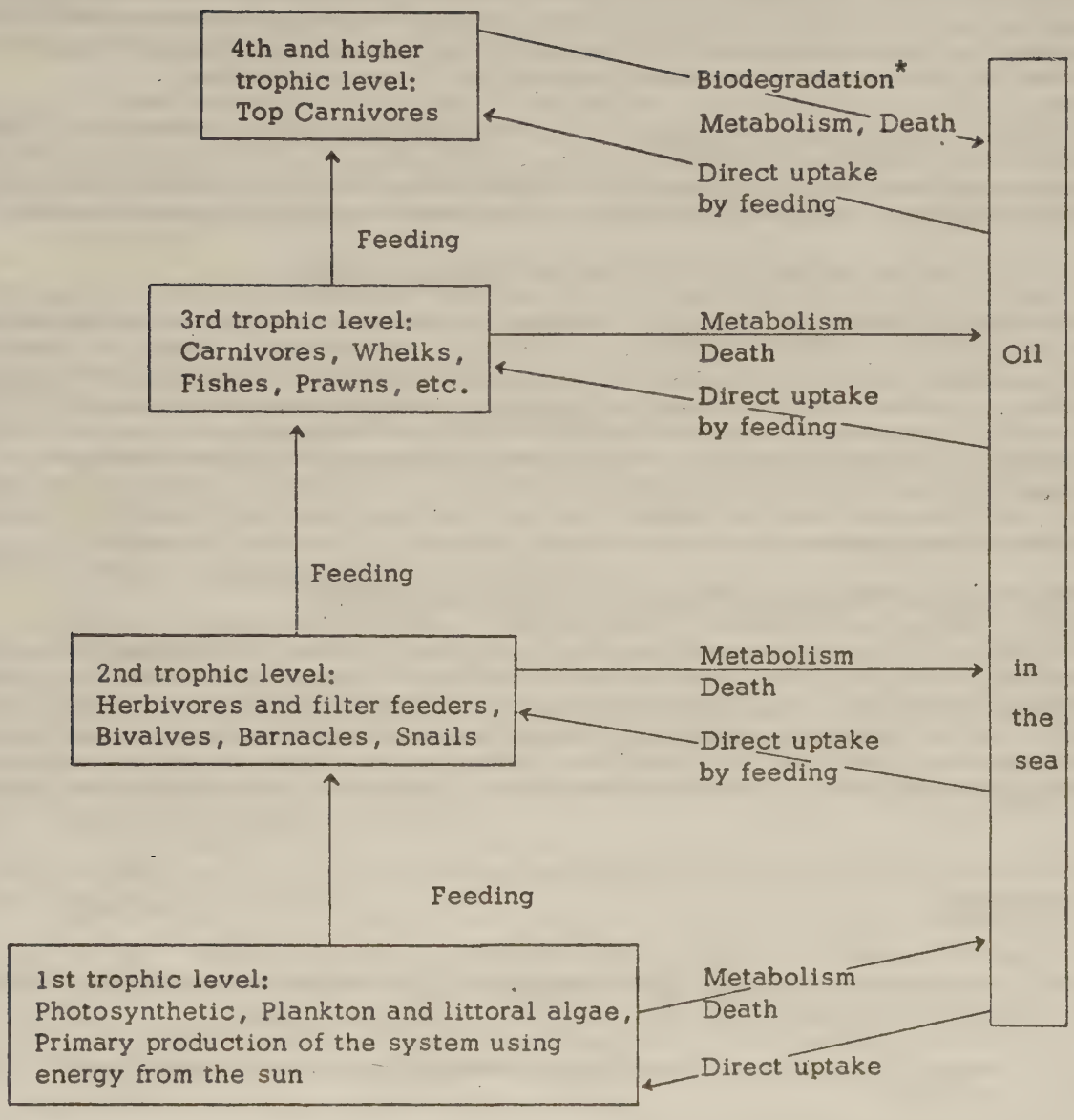


Figure 4: Possible oil concentration mechanisms in the ecosystem

(Arrows indicate possible movements of oil in the system)

Efficiency of energy transfer from one trophic level to the next is approximately 2 to 4 per cent.

* Biodegradation occurs on all return steps; oil in the sea is also subject to this effect

3.6 Determination of polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons are of special interest because of their involvement in the carcinogenesis in animals and in man. While methods exist for their analysis in polluted air, the situation in polluted water, sediments and organisms (Cahnmann and Kuratsune, 1957; Suess, 1970) is far less favourable. In oils, a much more complex mixture of substituted polycyclic aromatics is present than in polluted air (Eglinton and Murphy, 1969). Some components of this mixture may interfere with the determination of the biologically active aromatics, because of flurescence quenching or of spectral overlap.

Polynuclear aromatics have been isolated from crude oil and oil fractions by exact but slow isolation techniques (Carruthers et al., 1967) and more rapid determinations have been carried out by less reliable methods (Graef and Winter, 1968). The development of fast and reliable methods to determine the multiple carcinogens in oils is urgently needed.

3.7 Interaction between oil pollution and other pollutants

The solvent properties of fossil fuels and of oil products lead to the concentration in oil films of other non-polar compounds, both natural and man made. Little is known about synergistic effects of oil pollution and other non-polar materials. Through concentration by oil, other pollutants might be made available to organisms which are not normally exposed to them. Conversely, the accumulation of petroleum hydrocarbons in natural surface films, consisting of triglyceride and other lipids, might make the hydrocarbons more readily available than if they were present as tar lumps. Analytical studies of the composition of oil from tar balls and natural surface films and waxes are required to assess the magnitude of the problem.

4. REGISTRY OF LABORATORIES ACTIVE IN OIL POLLUTION RESEARCH

A registry of laboratories active in oil pollution research is being maintained by the Librarian, Marine Biological Association of the United Kingdom, The Laboratory, Citadel Hill, Plymouth, U.K. It is suggested that inquiries be directed to this laboratory; also laboratories not yet registered there should make their addresses known. The same organization will appreciate receiving reprints of all papers in this area for inclusion in their comprehensive pollution file. Reprints received will be indexed in the Marine Pollution Bulletin.

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Panel 3: INORGANIC CHEMICALS

D. Dyrssen (Chairman)
C. Patterson
J. Ui
G.F. Weichart

1. INTRODUCTION

Most elements in the periodic table are metals. Some of them are highly toxic (e.g., heavy metals); many are industrially produced in large quantities and their natural concentration levels in sea water are quite low in many cases (see Table I).

Mercury and lead are considered to be the most threatening pollutants (category I in Table I). They are, therefore, treated below under separate headings in the introduction. In the case of lead, the concentration in the surface waters of oceans in the northern hemisphere has increased by a factor of 5-10 above natural levels (Patterson, 1971). However, the effects upon the marine environment of this increase of lead is unknown. A similar increase in the concentration of mercury in sea water has not yet been shown.

The other elements listed in Table I are considered to be potentially harmful to the marine environment for different reasons. In some cases (e.g., Cu, CN, P and As) serious dumpings have occurred with harmful effects on marine life (fish kills, green oysters, red herring, etc.). In other cases the dumpings give rise to finely divided solid material (iron and aluminium oxides), which cause harmful slime excretion in shellfish. A third reason for introducing an element in Table I is that it is highly toxic and produced in large quantities. For these elements their possible entry into the marine environment should be considered and the levels in the sea measured. Titanium dioxide and cadmium are used in considerable quantities by plastic industries; sooner or later the products become waste. Vanadium is present in fossil fuels and can thus be introduced in the marine environment through the atmosphere. A balance sheet for the highly toxic beryllium has, to our knowledge, not been made. The pollution categories I-IV in Table I reflect the general feeling of the panel group. Another group of people might arrive at a slightly different order of importance. Some borderline cases have been left out. The acid oxides of nitrogen and sulphur, which are introduced with the atmosphere in the order of 50-80 million tons per year, by the burning of fossil fuels, will not change the pH of sea water to a measurable extent (the alkalinity of the sea corresponds to 130×10^{12} tons of SO_3). Oxidation in the sea water should eliminate their toxic effects. They have, therefore, been left out as well. The production of hydrogen sulphide can be a serious coastal pollution problem where sea water containing sulphate is reduced by large amounts of organic matter in sediments and stagnant waters. Although produced by organic pollutants hydrogen sulphide is often considered as an inorganic pollutant.

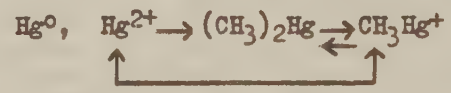
The routes of entry of inorganic pollutants are unknown in many cases, and the paths indicated in Table I can only be regarded as a rough evaluation. Atmospheric pollution may give rise to a world wide contamination of the seas (A in Table I), while dumpings, rivers, pipelines have mainly local or regional effects however serious they may be. In some cases large regions like the Baltic, the North Sea or the coastal area of Japan are affected. The equilibrium forms of the elements suggested in Table II may not include all the significant species of the elements because of their possible interaction with organic and inorganic particulates as well as with dissolved organic complexing substances.

1.1 Mercury

Typical values of mercury concentrations in surface sea waters are 0.13 - 0.15 µg/l. In deep waters the concentrations are about 0.3 µg/l (Hosohara, 1961, and Westermark, personal communication). The average concentration of mercury in sea water is usually quoted as 0.03 µg/l (Goldberg, 1963). This discrepancy calls for further investigation. Surface sea waters containing more than 0.2 µg/l have been considered to be contaminated with mercury. In the Minimata Bay values as high as 1 to 10 µg/l were measured.

Since the two tragedies of Minamata disease (Hosokawa et al., 1956; Kurland et al., 1960; Ui, 1967) and following several discoveries of local and regional mercury pollution (in the U.S.A., Sweden and other countries), mercury pollution of marine life became an urgent problem. The use of mercury in various forms has increased rapidly during recent decades (Keckes and Miettinen, 1970; Löfroth, 1970). World production of mercury is about 9 000 tons/year and about 5 000 tons/year is estimated as the artificial input into the ocean through various routes (Goldberg, 1970a). This artificial input is uneven, and has caused various local and regional mercury pollution such as: Minimata disease from use of mercury in chemical industry in Japan (Irukayama, 1967; Ui, 1966); elevated mercury levels in fish and water birds by paper and pulp industry in Scandinavian countries (Johnels et al., 1967; Keckes and Miettinen, 1970); accumulation of mercury in eel in Holland from the river Rhein (Ui, 1969), elevated mercury level in Canada (Sprague and Carson, 1970), in Italy (Ui and Kitamura, 1969) etc.

In the marine environment, most mercury compounds, except alkyl mercury, decompose to the inorganic form (Hg metal, $HgCl_4^{2-}$, HgS). Inorganic mercury then gradually changes into methyl mercury, which is very toxic and has a high tendency to accumulate through the food chain (Jensen and Jernelöv, 1969). In addition to the widely known acute and chronic toxicity of methyl mercury, the possibility of a genetic and teratogenic effect has been reported (Ramel, 1967; Skerfving et al., 1970).



Various factors which influence the accumulation of mercury in the food chain and the proportion between methyl and total mercury are the trophic level in the marine environment (Johnels et al., 1967, Ui, 1967) and perhaps temperature (Westöö and Rydälv, 1969; Ui and Kitamura, 1969). As mercury in fish exists to a high degree as methyl mercury and this compound has properties differing from those of inorganic mercury compounds, it is often necessary to analyse the methyl mercury content as well as total mercury content to get a correct understanding and evaluation of the situation.

Present monitoring systems and surveys have almost been entirely restricted to the analysis of biological samples; in most cases, from the point of view of food hygiene. The following figures might be given as a rough index for possible pollution:

	Unpolluted (ppm wet weight)		Polluted (ppm wet weight)	
Fish	(Sweden)	< 0.05	> 0.2	(Swedish Gov., 1968)
	(Italy)	< 0.1	> 0.5	(U.S.A. and Canada)
			> 0.2	(Ui and Kitamura, 1969)
	(Japan)	0.1	> 1.0	(Japanese Gov., 1970)
Feather of aquatic fowl (Podiceps crist.)		< 4	> 4	(Johnels et al., 1967)
Hair of fishermen (Japan)		6 ~ 10	> 20	(Japanese Gov., 1970)
" " " (Italy)		< 3	> 3	(Ui and Kitamura, 1969)

Remark:

Natural background seems to be influenced widely by the position of the species in food chain, e.g., sharks and tunas from Indian and Pacific Oceans showed rather constant total mercury contents of about 1 ppm dry weight (Japanese Gov., 1970).

1.2 Lead

Lead is a trace element, averaging 12 ppm in the earth's surface rocks. It is an enzyme inhibitor, and impairs cell metabolisms in the body (Hernberg et al., 1970). Man now uses lead on an industrial scale that greatly exceeds the natural flow of lead into the main sedimentary cycle. Lead concentration profiles in the oceans exhibit highly variable concentrations (0.07 to 0.4 µg Pb/l) in young surface waters, increasing with proximity to industrialized coasts, and they exhibit low uniform concentrations in ancient deep waters (0.02 µg Pb/l). Chemically analogous metals that are not used industrially on large scale such as barium and radium, exhibit contrary relationships: low concentrations in young waters and higher concentrations in old waters (Tatsumoto and Patterson, 1963; Chow and Patterson, 1966; Patterson, 1971).

Lead is naturally introduced by rivers both as particulates that mainly settled out on the continental shelves, and in dissolved form that is incorporated in pelagic sediments as chemical precipitates. In prehistoric times 1.3×10^{10}g of dissolved lead was chemically precipitated annually in pelagic sediments together with 0.5×10^{10}g of lead in settled silicate particles. Today, 20×10^{10}g dissolved lead enters the oceans annually from rivers, and a similar amount is introduced from the atmosphere by washout of aerosols originating from leaded automobile fuels (Tatsumoto and Patterson, 1963; Patterson, 1971).

Man has polluted the mixed layer of the oceans of the northern hemisphere with industrial lead so that average lead concentrations have been elevated by a factor of about five.

The adverse effect of this pollution on marine life is not known, although lead is known to interfere with the normal biochemical reactions in plant cells (Koeppe, 1970), and lead concentrations have probably been elevated in higher organisms near the end of marine food chains. The accumulation of industrial lead in surface layers of near-shore sediments has elevated lead levels in shellfish (Monier-Williams, 1938). These sediment residues cannot be removed and are introducing hazardous amounts of lead into shellfish.

In 1940 world lead production was 1.9 million tons, with 36 thousand tons being burned in leaded fuels. In 1966 world lead production was 3.5 million tons, with about 3 10 thousand tons being burned in leaded fuels. The production of silver is closely connected with the lead production and the rising prices of silver should, therefore, make it possible to open additional lead mines. They will then further accelerate industrial lead production, resulting in increasing lead pollution.

TABLE I

Inorganic Chemicals to be considered as Pollutants of the Marine Environment

Element 1/	Natural conc. in sea water 2/ µg/l	World production tons/year 3/ (1968)	Routes of entry into the sea 4/	Pollution categories 5/
H (acids)	pH=8 (alk.=0.0024 M)	?	D,A	III c
Be	0.001	250	U	IV c ?
Ti	2	1 000 000	A ?	IV b ?
V	2	9 000	A	IV a ?
Cr	0.04	1 500 000	R(U)	IV c ?
Fe	10	480 000 000	D,R	IV c
Cu	1	5 000 000	D,R	IV c
Zn	2	5 000 000	D,R	III c
Cd	0.02	15 000	A,R	II c
Hg	0.1	9 000	A,R	I b
Al	10	8 000 000	D,R	IV c
CN^-	-	?	D,R	III c
Pb	0.02	3 000 000	A,R	I a
P	-	?	D	IV c
As	2	60 000	D	II c
Sb	0.45	60 000	U	IV c ?
Bi	0.02	3 800	U	IV c ?
Se	0.45	1 000	U	III c ?
F^-	1 340	1 800 000	D,R	IV c

1/ Listed in the order of groups in the extended form of the periodic table

2/ These values are approximate, but are representative for low levels in unpolluted sea water

3/ From Minerals Yearbook

4/ D dumping, A through atmospheric pollution, R through rivers (runoff) or pipelines, U unknown

5/ I-IV order of decreasing menace; a worldwide, b regional, c local (coastal, bays, estuaries, single dumpings).

TABLE II

Equilibrium Species of Dissolved Inorganic Chemicals (elements) listed in Table I

Elements	Equilibrium species (reaction)
H (acids)	$HCl + HCO_3^- \rightarrow H_2O + Cl^- + CO_2$ $H_2SO_4 + 2HCO_3^- \rightarrow 2H_2O + SO_4^{2-} + 2CO_2$
Be	$Be(OH)_2$, solubility of BeO approx. 10 µg/l
Ti	$Ti(OH)_4$, solubility of TiO_2 unknown (low)
V	VO_3OH^-
Cr	$Cr(OH)_3$, solubility of Cr_2O_3 unknown (low) Chromate in waste should be reduced: $2CrO_4^{2-} + 4H^+ + H_2O \rightarrow 2Cr(OH)_3 + \frac{3}{2}O_2$
Fe	$Fe(OH)_3$, solubility of FeOOH approx. 5 µg/l
Cu	Cu^{2+}, $CuOH^+$, $CuHCO_3^+$, $CuCO_3$ (probably main form), $CuCl^+$, complexed also by dissolved amino acids
Zn	Zn^{2+}, $ZnOH^+$, $ZnCO_3$, $ZnSO_4$, $ZnCl^+$ (probably main form)
Cd	$CdCl^+$, $CdCl_2$, $CdCl_3^-$ (the last two are probably the main forms)
Hg	$HgCl_2$, $HgCl_3^-$, $HgCl_4^{2-}$ (main form)
Al	$Al(OH)_3$, solubility of Al_2O_3 approx. 300 µg/l
CN^-	HCN (90%), CN^- (10%)
Pb	Pb^{2+}, $PbOH^+$, $PbHCO_3^+$, $PbCO_3$, $PbSO_4$, $PbCl^+$ (probably main form)
P	Red phosphorous reacts slowly to phosphate $H_2PO_4^-$ and HPO_4^{2-}
As	As_2O_3 is oxidized to $HAsO_4^{2-}$
Sb	$Sb(OH)_6^-$
Bi	$Bi(OH)_3$, solubility of Bi_2O_3 is unknown (low)
Se	SeO_4^{2-}
F	F^- (50%), MgF^+ (50%)

2. METHODS

Riley (1965) has given a general survey of the analytical chemistry of sea water. Strickland and Parsons (1968) only treat manganese, iron and copper. The hexone (MIBK) extraction with ammonium pyrrolidine dithiocarbamate (APDTC) and subsequent analysis with atomic absorption spectrometry is used by many laboratories and the method is, therefore, treated separately below. Multi-element analysis is also treated separately. A new book by Jeffrey (1970) should be a helpful reference for the analysis of sediments. Marine organisms are usually dissolved by reflux boiling with nitric acid (Riley, personal communication), but low temperature dry ashing with microwave-activated oxygen is helpful in some cases. Enrichment (concentration) procedures of trace elements involve coprecipitation (Riley, 1965), solvent extraction, anion exchange (Zn, Cd, Tl and Bi) and the use of chelating ion-exchange resins (Riley and Taylor, 1968). Sampling techniques are very important for trace element analysis; it is easy to obtain too low values by adsorption on the walls of the sampling vessel and settling of particulate matter as well as obtaining high values by contaminating the sample (Riley, 1965). In general sampling techniques for the methods cited below are described in the literature. The techniques for lead are treated to some extent below. Recent intercalibration tests (Brewer and Spencer, 1970) have shown that most trace element analyses are quite unreliable. Recent work on water analysis has been reviewed by Fishman and Robinson (1969).

2.1 Dithiocarbamate extraction and atomic adsorption determination of heavy metals

Pyrrolidine dithiocarbamate is one of the most stable of the dithiocarbamates (Hulanicki, 1967). It reacts with all sulphide-forming metals, among which are Fe, Cu, Zn, Cd, Hg, Pb, As, Sb, Bi and Se in Table I. Hexone belongs to the type of solvents that burn well in a premixed flame. It is, therefore, a suitable organic solvent for extraction of the metal dithiocarbamates and subsequent analysis by atomic absorption spectrophotometry. Solvent extraction is also a good method for the necessary concentration of the trace metals. Separation by addition of masking agents or careful control of pH is not needed since atomic absorption is selective for each element. In principle only the dissolved elements will be extrated, but a variable amount of the elements in particulate and complete forms may be leached out. In addition, less hydrophilic particles may be transferred into the organic layer. The sea water samples are, therefore, often filtered. Without careful purification of chemicals, filters, glassware, etc., determinations of concentrations at the ppb level (µg/l) in sea water will be uncertain, and for elements like cadmium, mercury, lead and bismuth at the sub-ppb level the method can hardly give reliable results.

Determination of iron, cobalt, nickel, copper, zinc and lead in sea water have been reported by Brewer et al. (1969), Burrell (1967), Brooks et al. (1967a) and Magee and Rahman (1965).

Recently, Burrell and Wood (1969) used the tantalum boat technique for the direct determination of zinc in sea water by atomic absorption; contamination problems have been shown to be severe for zinc.

2.2 Multi-element methods

There are essentially three methods of analysis that may be considered for multi-element analysis, namely neutron activation analysis, mass spectrometry, and emission arc, spark or flame spectrometry. The two first methods are very sensitive, and thus careful work is needed to avoid false results.

Sea water samples in general cannot be analysed for trace elements directly by these methods because of the large background of sea salts (mainly sodium, potassium, magnesium, calcium, chloride and sulphate). The trace elements have, therefore, to be separated from the main constituents by coprecipitation, solvent extraction, chelating resins according to Riley and Taylor (1968) or selective ion-exchange sorption according to Samsahl et al. (1968).

Neutron activation analysis in oceanography was treated by a NATO sub-committee in 1968, and recently Lutz at NBS has put out a bibliography. Earlier Schutz and Turekian (1965) investigated several trace elements in sea water by this method. The neutron activation analysis of lanthanide elements in sea water has been reported and reviewed by Högdahl et al. (1968). Mass spectrometry has been treated by Ahearn (1967). The use of mass spectrometry in connexion with isotope dilution analysis of sea water has been treated by Chow (1968).

The use of modern emission spectrography for heavy metal analysis in soils and water has been described by Danielsson (1970). Riley (to be published) has used pulse polarography to determine several trace elements simultaneously.

Multi-element analysis may reveal unexpected pollution of the marine environment. Patterns of elements give important information on "unnatural" distribution of the elements. Point by point investigation of solid or organic matter by use of electron or laser beams may reveal unexpected concentrations of certain inorganic pollutants.

2.3 H (acids)

Dumpings of acid waste and acidic effluents from pipelines and rivers can be detected locally by pH measurements according to Strickland and Parsons (1968, p.29-31). A new pH-scale with buffers solutions of different salinities is being worked out at the Department of Analytical Chemistry, University of Gothenburg by Dyrssen et al.

2.4 Be (beryllium)

The beryllium concentration in sea water is supposed to be quite low (see Table I) and enrichment by coprecipitation with TiO_2 or solvent extraction with a beta-diketone, e.g., acetylacetone or TTA in chloroform (Jeffrey, 1970) is necessary. Fluorimetric determination with morin (Jeffrey, 1970) is a sensitive method, but interferences are not unlikely to occur. The detection limit for the beryllium determination by atomic absorption spectrophotometry is rather low (Angino and Billings, 1967), but mass spectrometric analysis will probably be preferred in the future.

2.5 Ti (titanium)

Atomic absorption spectrometry is not very sensitive for titanium, and thus spectrophotometric analysis based on some reagent like diantipyrylmethane (Jeffrey, 1970) is preferable. Even if the concentration of titanium is not very low in sea water (2 µg/l) a concentration step is needed, e.g. by coprecipitation with iron (III) hydroxide. The iron must then be reduced in order not to interfere with the reaction. Isotope dilution analysis has been used for direct determination of titanium in polar snows at concentration levels of 0.01 µg/kg (Murozumi et al., 1969).

2.6 V (Vanadium)

Similar as for titanium. Chan and Riley (1966) used diaminobenzidine as a reagent; the iron carrier was removed by cation exchange. N-benzoyl-o-tolylhydrozylamine has also been used as a reagent for vanadium (Jeffrey, 1970).

2.7 Cr (chromium)

The level of chromium is low in sea water. The reactions of Cr (III) in aqueous solution is sluggish. Chelex-100 retains chromium (III) only partially (Riley and Taylor, 1968) and coprecipitation with iron hydroxide and subsequent neutron activation analysis may give the best result. Further work is needed.

2.8 Fe (iron)

The different methods for the determination of iron have been treated by Riley (1965). The following method is used at Hamburg (Weichart, personal communication) for polluted sea water. 50 ml of sea water are acidified by some 1 M HCl. After 30 minutes the iron (III) is reduced by hydroxylammonium chloride. After a reaction time of 5 minutes the pH is brought to 4.0 - 4.5 by addition of sodium acetate. Then 1, 10 - phenanthrolinium chloride is added. The extinction of the solution is measured by a filter photometer with a filter S 47 or by a spectrophotometer at 492 nm. Humic acids interfere with the determination according to Koroleff (1968).

2.9 Cu (copper)

Copper in sea water is analysed by the APDTC-MIBK method of Brooks et al. (1967b), Burrell (1967), Brewer et al. (1969) and Magee and Rahman (1965). The chemistry of copper in natural aqueous solutions has recently been reviewed by Rickard (1970).

2.10 Zn (zinc)

Zinc in sea water is analysed by the APDTC-MIBK method by Brooks et al. (1967b), Brewer et al. (1969), and Burrell (1967). Direct determination by atomic absorption has been used by Burrell and Wood (1969). Ionic zinc in sea water has been determined electrochemically by Macchi (1964).

2.11 Cd (cadmium)

The dithizone chloroform extraction method has been used by Mullin and Riley (1956), but the APDTC-MIBK atomic absorption method is a useful alternative (Yamagata and Shigematsu, 1970) for polluted wastes.

2.12 Hg (mercury)

The following three methods have been widely used to measure total mercury concentration in various samples:

a) colorimetry with dithizone (Keckes and Miettinen, 1970) is available in common laboratories. The sensitivity is around 1 µg/ml; with enrichment the limit is around 10 ng/ml.

b) Flameless atomic absorption spectrophotometry (Kalb, 1970; Lindstedt, 1970; Manning, 1970; Keckes and Miettinen, 1970) has become popular in modern laboratories. The sensitivity is around 10 ng/ml; with careful concentration the limit is 0.2 ng/ml (Keckes and Miettinen, 1970).

c) Activation analysis by neutron radiation (Sjöstrand, 1964; Ishida et al., 1970; Keckes and Miettinen, 1970) is suitable for large numbers of samples. The method is limited by equipment sensitivity at approximately 50 ng/ml; with enrichment and chemical separation the limit is about 0.1 - 0.01 ng/ml (Westermark and Sjöstrand, 1960).

For organic mercury compounds solvent extraction and gas chromatography has proven to be effective (Westöö and Sumino, reviewed by Keckes and Miettinen 1970). The most important species are methyl and other lower alkyl mercury compounds, phenyl mercury, and in some cases alkoxy mercury and dimethyl mercury. The sensitivity with electron capture detector is 10^{-13} g for CH_3HgCl (Westöö, 1966) and 10^{-11} g for C_6H_5HgCl has been reported by Sumino (1968). Dilute mercury solutions have been studied by Toribara et al. (1970), and the speciation of mercury in natural waters has been calculated by Anfält et al. (1968). A new method for the determination of mercury in the marine environment has recently been worked out by Murray and Riley (1971).

2.13 Al (aluminium)

Spencer and Sachs (1969) have studied particulate aluminium in sea water by atomic absorption. Sugihara and Yamamoto (1968) determined traces of iron and aluminium in sea water by oxine extraction with chloroform after acid digestion of the sample. The inference with fluoride was prevented by adding beryllium. The absorbence of the chloroform extract was measured at 390 (410 nm according to Jeffrey, 1970) and 470 nm. Probably cupferron extraction with hexone (MIBK) and subsequent analysis by atomic absorption using a dinitrogen oxide burner is preferable. Photometric determination with pyrocatechol voilet has also been used (Jeffrey, 1970).

2.14 CN (cyanide)

Recommended standard methods for analysis of waste water for cyanide are available (Society for Analytical Chemistry, 1967; American Public Health Association, 1965). This method has recently been adopted for use with the Auto-Analyzer (Casapieri et al., 1970). It remains to be shown, however, if the method also works for saline waters.

2.15 Pb (lead)

Most reported measurements of lead in sea water are inaccurate because contamination occurs during concentration steps of the analysis, and because the distribution of lead among dissolved and particulate phases in sea water is not understood (Chow, 1968). The most reliable method is isotope dilution, wherein a known amount of a stable lead isotope tracer is mixed with the seawater sample, aged for several weeks, acidified, withdrawn by means of solvent extraction and ion exchange, and subjected to isotopic analysis in a mass spectrometer (Tatsumoto and Patterson, 1963). The ratio of tracer to natural isotope and the weights of the tracer and sample yield the lead concentration. At concentrations below 0.1 µg/l, contamination severely limits accuracy, and errors from this source amount to about 25 percent of the amount present at 0.03 µg/l. A double spiking method which monitors extraction yields reduced contamination errors to about 25 percent of the amount present at 0.005 µg/l (Murozumi et al., 1969). Such errors become negligible at concentrations above 0.5 µg/l. The isotope dilution method may not detect lead tightly bound in particulate matter, and values reported by this method may be low for this reason. Studies of lead in filtered waters and in plankton are inconclusive, but indications from these experiments suggest that about half the total lead is in dissolved form in sea water.

Other methods of determination include spectrographic analysis of residues obtained by evaporation (Black and Mitchell, 1952), concentration by solvent extraction and colorimetric analysis (dithizone) (Loveridge et al., 1960) and concentration of solvent extraction (ammonium pyrollidine dithiocarbamate in methyl isobutyl ketone) and analysis by atomic absorption spectrophotometry (Brooks et al., 1967b). All of these methods, as utilized so far, give lead concentrations in surface waters that are ten times higher than the values obtained by isotope dilution methods. The ubiquity of lead contamination on shipboard, in the collecting operation, and in the laboratory, suggests that the higher reported values are incorrect because of contamination. This is indicated by the atomic absorption work (Brooks et al., 1967b), where a concentration profile showed lead remaining at 3-4 µg/l down to a depth of 1 000 metres. This contrasts with a number of profiles studied by isotope dilution (Tatsumoto and Patterson, 1963) at locations near those of the atomic absorption study, which showed 0.2 to 0.4 µg/l at the surface, declining to 0.02 to 0.03 µg/l at 1 000 metres depth, below which concentrations remained fairly uniform.

Future investigations of lead in sea water should be made with extreme care to prevent contamination. More attention and study should be given to blank levels for sample collecting and the analytical methods, than to the measurements of sample concentrations, for the latter are meaningless unless contamination is absolutely controlled and understood. Descriptions of blank determination methods and contamination controls in Tatsumoto and Patterson (1963) and Murozumi et al. (1969) should be read carefully and suitable adaptations of those techniques should be made before analysis is attempted. A check on the overall analytical method would be an analysis of a deep water sample at one location. If values less

than 0.1 µg/l are not obtained for the deep water sample, contamination during collection or analysis that has not been accounted for is indicated. There are indications that thin oily layers on water surfaces may contain excessive amounts of lead. Future sampling techniques should be adapted to study this possible phenomenon. Up to now, filtering techniques have not been satisfactorily worked out as a means for studying dissolved and particulate lead. Future analyses should include attempts to improve knowledge in this field, because proper understanding of the speciation of lead in sea water stands as the next major advance in the marine chemistry of lead. It seems likely that these future investigations will require major expenditures of time and money, since repeated trials, reassessments, and modifications of the experiments will have to be made before satisfactory data can finally be obtained.

2.16 As (arsenic)

Portmann and Riley (1964) have developed a method for the determination of arsenic in both sea water, marine plants and sediments. Arsenic in sea water is recovered by coprecipitation with thionalide, and this procedure has been applied to silicate material by Jeffrey (1970). The molybdenum blue reaction is used for the determination. An alternative spectrophotometric method is based on the reaction with silver diethyldithiocarbamate (Jeffrey, 1970) and the corresponding zinc salt is used for the substoichiometric determination (Hulanicki, 1967). Arsenic in organic material is also determined by activation analysis (Sjöstrand, 1964).

2.17 Sb (antimony)

Antimony in sea water has been determined by Portmann and Riley (1966b). They used coprecipitation with manganese dioxide. After separation from manganese it was determined spectrophotometrically by extraction of the Rhodamine B complex. Neutron activation analysis has been used by Schutz and Turekian (1965).

2.18 Bi (bismuth)

Portman and Riley (1966a) have reported a method for the determination of bismuth in sea and natural waters. The concentration of bismuth in sea water is low and the method of extraction with dithiocarbamate, and subsequent analysis with atomic absorption spectrometry, will need a fairly large concentration step and cause similar difficulties as have been met with lead. However, the background disturbance should be less severe, and any serious pollution should be possible to detect.

2.19 S (hydrogen sulphide)

Fonselius (personal communication) has a working methylene blue method for Baltic and Black Sea waters. This method which is based on N, N-dimethyl-p-phenylenediamine is only slightly different from the one given by Strickland and Parsons (1968).

2.20 Se (selenium)

A method for the determination of selenium in sea water, silicates and marine organisms has been published by Chau and Riley (1965).

2.21 F (fluoride)

Brewer et al. (1970) have used both the lanthanum-alizarine complexone method (Greenhalgh and Riley, 1961) as well as the fluoride electrode. A computerized standard addition method using the same electrode has been worked out by Anfält and Jagner (1971). Extensive studies of fluoride in the North Atlantic have been published by Bewers (1970), and similar studies of the Baltic have been made by Sen Gupta (1970). They both used the Greenhalgh-Riley method.

3. RECOMMENDATIONS

3.1 Production, consumption, pathways of disposal

It is necessary that data on world production of the toxic inorganic chemicals mentioned in Table I, together with consumption and waste disposal patterns, be collected and organized in a form useful for evaluation of pollution hazards. In the past it has been difficult to acquire such data because producers and users have not been requested to furnish it to the world public. It should be recognized that when pollution extends to a world-wide scale, it should become an obligation to furnish production and dissemination data to international bodies.

3.2 Research and analytical methods

In the past important development in analytical techniques have been made by investigators studying basic problems in nature; therefore further research should be encouraged along basic lines, rather than simply promoting the gathering world-wide data with existing methods which may be inadequate. Knowledge of natural levels of the toxic inorganic trace elements mentioned in Table I in the marine environment and biosphere is needed and can be acquired by encouraging studies of the natural pathways of these elements through the seas and biosphere. Studies of the distribution of pollutants in various phases of the biosphere would better reveal the sources and pathways of pollution, and thus help to eliminate it. A need is recognized for an immediate improvement of existing analytical techniques in the following categories: methods for distinguishing between various forms of the elements, multielement and automatic analysis; and simple but reliable techniques which do not demand the use of expensive equipment.

3.3 Biological response

Classical methods of detecting and describing the poisonous effects of toxic metals such as mercury and lead are now recognized as being inadequate in that they dealt in the past with gross morphological features of tissue lesions and organ disfunctions. Today, more subtle effects such as enzyme inhibition and teratogenic effects within cells, which cause disruption of biochemical processes, are being discovered. Increases by industrial pollution of toxic metals in the marine environment should be regarded with concern and not evaluated according to criteria established in the past. The effects of toxic metals on various phases of marine food chain should be studied at biochemical levels, and it is recommended that such studies be encouraged. Investigations of detrimental effects of long-term exposures of heavy metals should also be encouraged.

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Panel 4: ORGANIC CHEMICALS

G.G. Widmark (Chairman)
W.D. Garrett
K.H. Palmork

1. INTRODUCTION

This report discusses the general problems of organic chemicals as pollutants in the marine environment. Although this is a broad and important field, it has been only superficially investigated. Since all organic compounds are assumed, in some way, to affect the toxins, and all organics sooner or later will demand oxygen upon decomposition, no emphasis has been put on BOD and toxins. A selection of organic chemicals found or expected to be found in sea water are tabulated in this report. This selection is neither considered to be complete nor to give any indication of the possible harm of these potential pollutants to the marine environment. Two other panels are considering the specific problems of chlorinated hydrocarbons and petroleum. Thus, these two fields are largely excluded from this report.

2. ORGANIC CHEMICALS

By traditional definition organic chemicals are those which contain carbon. A few one-carbon-atom compounds such as CO_2 and CO are an exception to this definition and are not considered to be organic. At present the chemical literature describes over one million organic compounds, and this number is small when compared to the structural variation possible within a few classes of organic compounds.

Since the specific ability of carbon to bind with other carbon atoms is the essence of organic chemistry, some organic chemists refer to the nature of this bond when defining organic chemistry. By synthetic techniques a number of non-carbon containing compounds having organic type bonds are known. However, these non-carbon organics are not yet considered to be of importance to marine pollution.

2.1 Organic chemicals as pollutants

Organic pollutants are characterized by their complexity. Therefore, individual organic pollutants are not easily distinguishable above the background of the naturally occurring organic components of the sample. There are some apparent exceptions to this statement which have been overemphasized. Polychlorine containing organic compounds such as DDT and its homologues give marked and clear responses on electron capture detectors. This is true even when large amounts of non-capturing compounds of the aliphatic type are present in the same fraction examined. However, even experienced laboratories might have considerable difficulties in distinguishing the DDT[1] type compound from those of other electron-capturing compounds such as the poly nuclear aromatic hydrocarbons.

The natural organic constituents of sea water are expected to be formed entirely by biological processes utilizing carbon dioxide as the basic source. Hence, when sufficient size of a sample is available, it might be possible to differentiate natural and synthetic organics by their C-14 content, provided that the latter are synthesized from fossil carbon, which is not always the case.

Some organic compounds are classified as pollutants because they are non-biodegradable whereas some other organic compounds are considered to be pollutants because they rapidly consume the dissolved oxygen of the water (high BOD). The oxygen consumption is an indication of a rapid biodegradation of the specific organic compound. The degradation may not necessarily proceed all the way to CO_2 but could slow down at some intermediate product. On the other hand, the products once formed from so-called non-biodegradable (slowly biodegradable) compounds might then rapidly and totally decompose into CO_2.

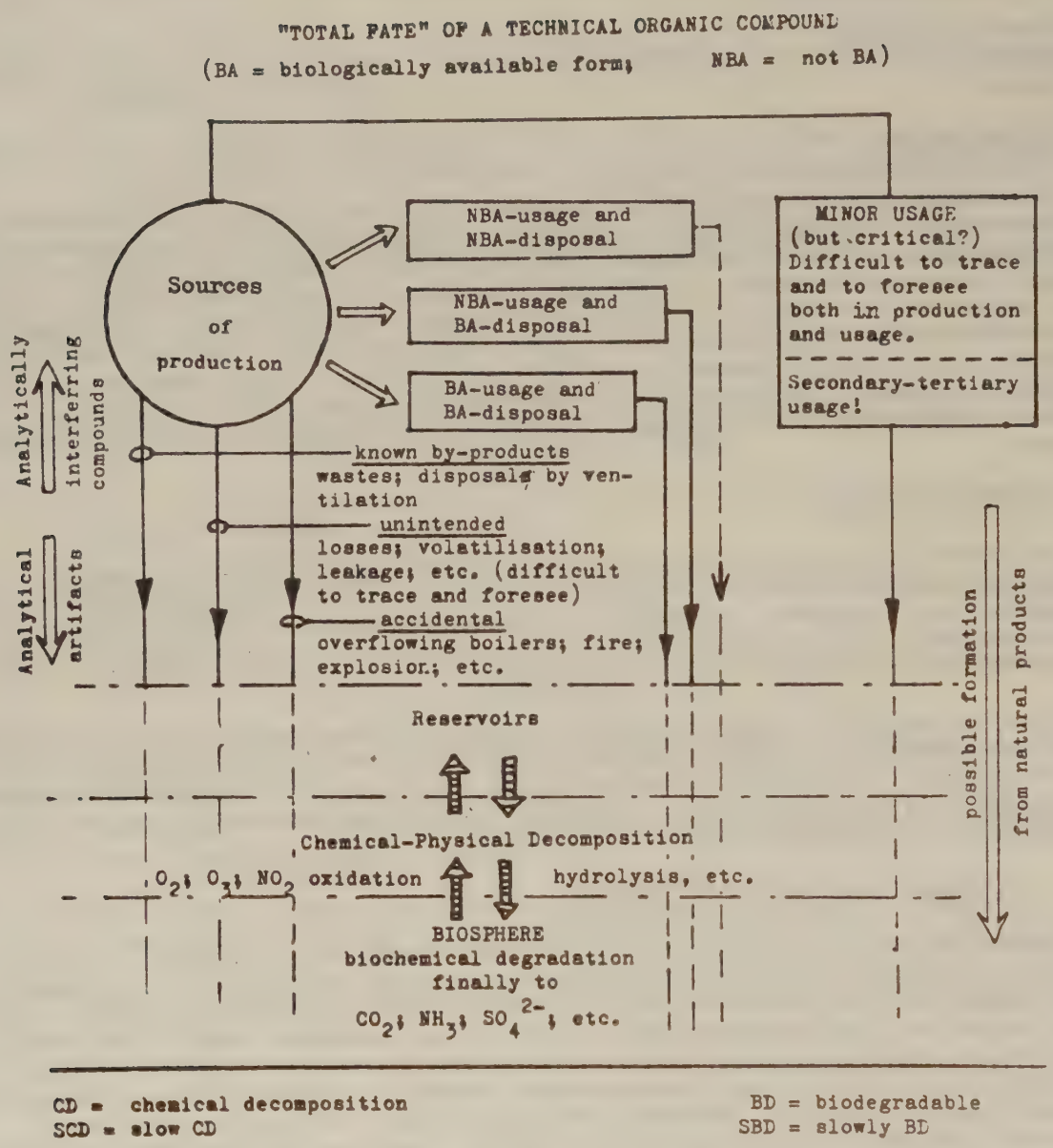

Figure 1: Total fate of an organic compound. Some pathways by which an organic compound is disseminated into the biosphere, and some types of reactions involved in the total decomposition of the organic compound and its metabolites.

Organic compounds present in the marine environment will be decomposed as well by pure chemical-physical degradation. Reactions of this type, such as radiation induced oxidation by O_2, O_3, NO_2, etc., are assumed to contribute in particular when the water is temporarily evaporated, as in wind spray. Thus, when searching for the "total fate" of organisms, i.e. pathways by which organic compounds are decomposed totally in the sea, not only biochemical reactions are to be considered. An attempt is made in Figure 1 to illustrate items at a total fate study including also possible analytical artifacts.

2.2 Levels of concentration to be considered

There is a question as to whether a lower limit of concentration exists, at which the concept of pollution has no reality. With reference to the accumulation of DDT and PCB in the marine food chain, it has been stated that even the smallest amount of pollution is of importance to the marine environment. However, the analyst is generally not yet able to handle concentration levels below ppb although some water analyses have been reported at ppt and ppq levels. A satisfactory solution at present to the analytical problems of pollutant accumulation is to use the food chain to give concentrations exceeding those of the sensitivity of present analytical methods and then extrapolate to the "true" content of the water. Naturally, the increase of analytical sensitivity seems to be a direct approach to solve the problem. However, the great increase of possible constituents at tracer levels is demonstrated in Figure 2 (Widmark, 1971). It is recommended that a study be initiated to determine analytical procedures which are applicable to the lowest levels of concentration for those compounds of interest to environmental studies.

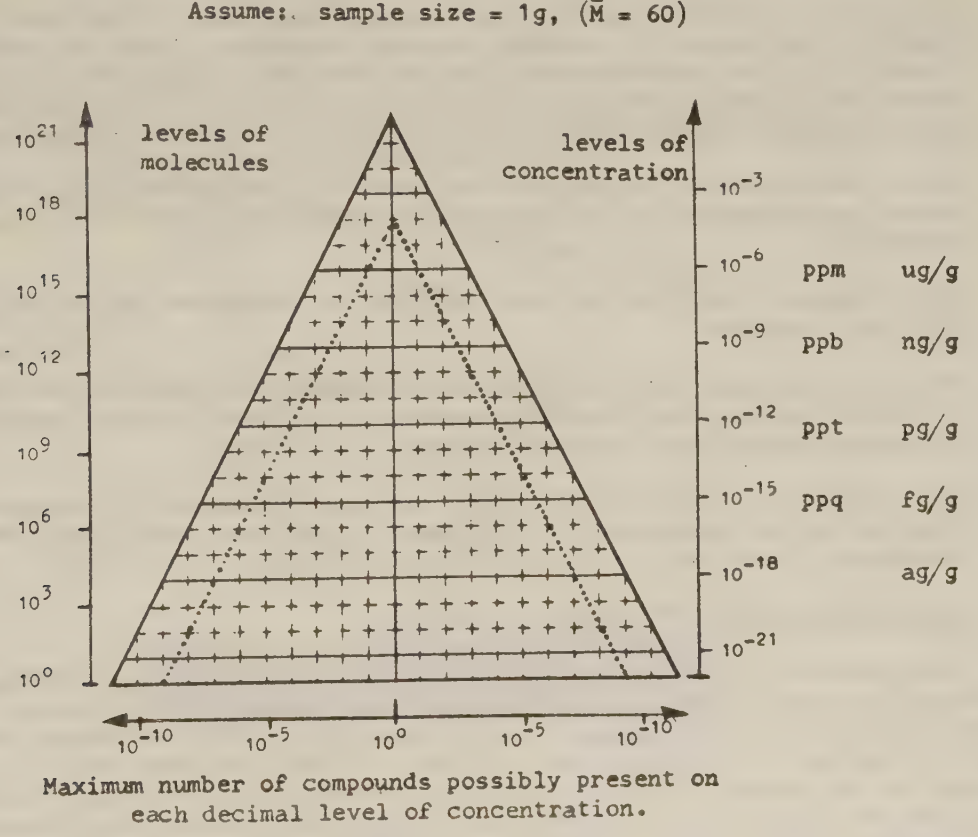

Figure 2: 'Map of Tracer Cosmos'. This figure demonstrates the large number of tracer compounds (therefore 'Tracer Cosmos') which might comprise the one percent impurity in a sample which is 99% pure. Note: Consider as an exercise the number of organic compounds which could be present in the 0.1% organic matter often obtained from ether extraction of a water sample.

To facilitate the demonstration, we assume a one gram sample with a mean molecular weight of 60. It is further assumed, as indicated by the dotted line, that all the tracer compounds (0.01g) are equally distributed on each decimal level of the concentration scale of the figure. Then, as an example, 100 compounds are present at the ppm level and 100 000 compounds at the ppb level. It seems extremely unlikely that the one percent impurity consists of only one single component, or is distributed only on the ppm level: then 10 000 compounds.

In conclusion, the characteristics of organic pollutants can be grouped as follows:

1. There exists an inexhaustive number of organic compounds that are being, or may in the future be synthesized. All of these might be classified as potential pollutants.

2. It is assumed that the behaviour of an organic compound will differ in response to various biological situations; thus making the exact definition of a pollutant difficult.

3. In general, the complexity of a sample is such that individual organic pollutants are not easily distinguishable from naturally occurring organic compounds.

4. In the marine environment, organic compounds are assumed to undergo a variety of types of reactions (biological and/or purely chemical). These reactions will increase the number of components (potential pollutants) but will not necessarily change the total mass (see Figures 1 and 2).

5. By stepwise reactions under natural oceanic conditions, a pollutant may be converted (partly) into naturally occurring organic compounds. These are usually not classified as pollutants unless they are present at concentration levels known to cause harm to the environment. In addition, indirect action has to be considered, e.g., the utilization of oxygen resulting in the reduction of sulphate into H_2S.

6. The ultimate fate of any organic pollutant is decomposition into carbon dioxide, water, and depending on its elementary composition, other simple inorganics (see Figure 2).

7. The pathways by which an organic pollutant is decomposed might vary considerably with the ecosystem.

8. Organic pollutants might be deposited in such a way (burial in sediments or occlusion in refactory particulate matter) that their further decomposition is retarded greatly (cf., fate of inorganic pollutants).

9. The transport of organic pollutants, and their decomposition products from the sea into the marine atmosphere is believed to occur more readily than the sea to air transport of inorganic pollutants (see Figure 3).

3. DESCRIPTION OF THE POLLUTANTS IN THE SEA

The oceans may be thought of as complex soup whose organic constituents may be categorized by chemical class and distribution in the marine environment. There are three primary categories of distribution. First, the water-soluble compounds are determined by methods for so-called dissolved organic carbon. This class represents the greatest percentage of the natural or background organic components of the sea. The second group may be considered to be partly soluble but highly surface active due to polar molecular characteristics. This group of compounds includes many lipids, and other materials which contain oxygen, nitrogen and sulphur whose balance between polar and non-polar properties creates a strong tendency to adsorb at phase boundaries. These surface active materials will be adsorbed on particulate matter in sediments, on air bubbles and at the air-sea interface. A third category, the hydrocarbons, are hydrophobic and largely water insoluble compounds.

These hydrophobic materials may be found at the sea surface or dispersed in insoluble form into the ocean and its sediments. It is the surface active compounds of category two which assist in the distribution of the hydrocarbons throughout the marine environment since their surface active properties lead to surface spreading, emulsification and in general a mixing of the dissimilar polar and non-polar species. Aggregations of organic material at the sea surface or on oceanic particulate matter will have the ability to acquire and concentrate other organic pollutants which are preferentially soluble in organic compounds. For example, the partition coefficient of DDT between sedimental river oils and water has been found to be 1.5×10^6 by laboratory experiments (Hartung and Klingler, 1970). Petroleum spills and natural sea slicks may hold lipophilic pollutants as DDT in thin layers at the sea surface where such pollutants can be incorporated and concentrated into the oceanic food chain through biological assimilation (Figure 3).

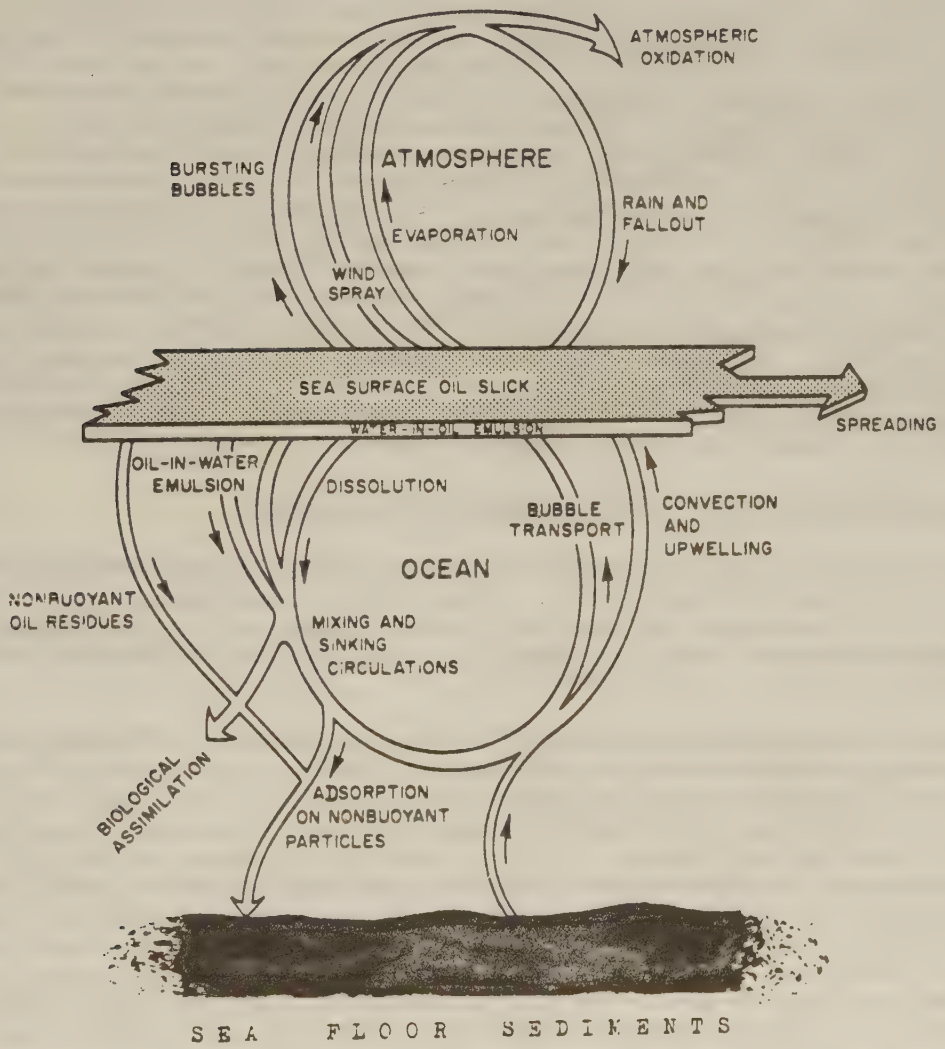

Figure 3.

In general, the background organic level of the sea is sufficiently large to mask detection of many of the introduced pollutants. However, when a contaminant or pollutant enters the sea locally its concentration may become considerably greater than that of the background and its influence upon environment correspondingly increased. The average level of total organic compounds is 1 mg/ml in the upper 300 m and 0.5 mg/l at greater depth. It has been estimated that 4.45×10^6 tons of petroleum products will be added to the world oceans per year by 1980 (Anon., 1970). Such pollution will be detectable as an increase in hydrocarbon level since it will occur in localized regions where its concentration will exceed that of the naturally occurring organic sea water components. Other pollution forms are detectable from the background organic level through appropriate concentration and isolation techniques, coupled with instrumental and other sensitive analytical techniques, e.g., gas chromatography, thin layer chromatography, spectroscopy, mass spectrometry.

3.1 Methods of entry into the marine environment

Many forms of organic chemicals are added to the ocean through human activity, some with deleterious effect to marine organisms. At the present time only a few have been clearly demonstrated to be harmful. The task remains to test the toxicity of these additives and develop suitable analytical methods for the isolation, detection determination and identification in sea water. Tables I through III list potential organic pollutants and natural organic oceanic constituents along with potentially useful analytical methods for their determination. This complex organic input enters the marine environment by a large number of pathways, and having reached the sea is dispersed or concentrated according to its chemical nature. Paths of transport into the sea include rivers, atmospheric circulation, ships' refuse, ocean industry, and intentional dumping. Once in the sea the organic pollutant may be further transported by oceanic circulations, sedimentation and biological transport. Some of these processes along with those which disperse surface organic films are depicted in Figure 3 (Garrett, 1970). An important conclusion from this drawing is that no point in the marine environment appears safe from contact with most pollutants. Between air, sea and the ocean floor there are numerous ways by which organic interchange may occur and it should be assumed that no ocean area is immune from potential harm.

4. ANALYTICAL METHOD FOR ORGANIC CHEMICALS IN SEA WATER

Selected methods for the analysis of organic compounds are reviewed in Strickland and Parsons (1968) and Golterman (1969). An additional comprehensive paper (Wagner, 1969) reviews analytical techniques and provides a useful commentary on the "Definition of dissolved organic carbon" as well as methods of isolation for the various classes of organic compounds.

Several methods have been developed for the determination of total, dissolved and particulate organic carbon in sea water. Most of them are based on wet oxidation, but according to many analysts, it is uncertain whether all types of organic compounds have been completely oxidized. The methods of carbon analysis in sea water have been thoroughly examined by Strickland and Parsons (1968). A recent instrumental method for dissolved carbon determination utilizes ultra-violet radiation using potassium peroxidisulphate as a source of oxygen. The carbon dioxide formed by the oxidation of dissolved organic compounds is absorbed in dilute sodium hydroxide solution and the change of the electrical conductivity in the base is proportioned to the amount of dissolved organic carbon. This procedure has been adapted to a commercial automatic analyser (Ehrhardt, 1969). By this method 0.1 mg of dissolved inorganic carbon may be detected in 1 litre of sea water with a standard deviation of 0.06 mg in the 1-10 mg C/l range. For comparison, the method recommended by Strickland and Parsons is useful in the 0.09-6 mg C/l range with a precision of 0.09 mg/l. From this information it is difficult to detect any great advantages of one method over the other. However, the automated system will require less manpower. Methods of automated elementary analysis (CHN) also allow the read out of organic nitrogen.

TABLE I

Some Compounds of Synthetic Origin to be considered in Pollution Studies (see 1. INTRODUCTION)

Compounds (Pollutants)	Comments
Alkylbenzene sulphonates (ABS)	Detergent of the "hard" type, toxicity to marine organisms increasing with increasing branching. Not readily biodegradable.
Linear alkyl sulphonates (LAS)	Detergent of the "soft" type, less toxic to marine organisms than the former and more rapidly degraded by biological organisms.
Phenols	In waste from industry, coke and gas works, also found in natural sea water (1-3 µg/l; Degens et al., 1964)
Polycyclic aromatic hydrocarbons	From oil refineries, heating, etc.
Aromatic amines, e.g., aniline	From dye industries
Surface active materials (in general)	Petroleum and chemical industry, many different compounds. May alter air-sea interactions and exchange processes, emulsifier for insoluble organics into the sea.
Phenoxyacids	Herbicide.
Insecticides of the organic phosphorous type.	Used in agriculture.
Insecticides of the carbamate type.	There is a trend to use more of this type of insecticides.
Quinones, diotins, etc.	Bleached kraft chlorination effluent from paper pulp industry contains among others tetrachloro-o-benzoquinone, toxic to young salmon (Das et al., 1969)
Nitriles and other nitrogen containing compounds.	Waste from plastic industry, dumped into the sea in barrels. Also waste from the production of explosives.
Organic phosphoresters, e.g., Tricresyl phosphate.	Waste from plastic industry, petroleum additives, etc.

TABLE II

Some Organic Compounds (Pollutants) of mainly Natural Origin
(see 1. INTRODUCTION)

Compounds (Pollutants)	Comments
Tannins	Waste from dye industry
Lignin	Waste from paper and pulp mill industry
Carbohydrates	Waste from paper and pulp mill industry, breweries, whisky industry and from sugar production. High BOD.
Proteins, peptides, amino acids, amines, fatty acids, lipids	Waste from slaughteries, dairies and fish industry. High BOD.
Hydroxy fatty acids, humic acids	Waste from the bark shipping of pine
Pyrenthrines	Insecticides
Terpenes	Flotation of ore, etc.
Polycyclic aromatic hydrocarbons (PAH)	Found in marine organisms and sediments, and in areas with volcanic activity (Suess, 1970).

TABLE III

Potentially Useful Analytical Methods for Organic Chemicals in Sea Water

Chemical Classes of Interest	Total Class Determination	Analysis of Specific Compounds within Class
Dissolved Organic Carbon	Ehrhardt, 1969 Menzel and Vacarro, 1964	-
Particulate Organic Carbon	Strickland and Parsons, 1968, pp 213-217 (ref. 1) Szekielda and Krey, 1965	-
Hydrocarbons	———	Blumer et al., 1970
Hydrocarbon gases	———	Swinnerton and Linnenbonn, 1969
Lipids, fatty acids	Mukerjee, 1956	Williams, 1961
Phenols, thiols	———	Kawahara, 1968
Polycyclic aromatic hydrocarbons	———	Degens et al., 1964
Carbohydrates	Strickland and Parsons, 1968, pp 173-174 (ref. 1)	-
Polypeptides, amino acid	Keeler, 1959	Palmork, 1969 Siegel and Degens, 1966
Volatile organics	———	Baker, 1966 Manadevan and Stenroos, 1967 Corwin, 1969

Table III reviews potentially useful procedures for the analysis of classes of organic chemicals and specific compounds in sea water. With the exception of the few methods which have been discussed, there are no well-defined, broadly-used analytical procedures for organic substances in sea water. This situation exists because only a handful of chemical oceanographers have become involved with organic sea water analysis, each with an interest in different chemical classes or groups of compounds. The references listed under specific compounds in Table III represent useful analytical procedures but are not recognized standardized techniques by the world oceanographic community. Some of these methods may eventually be selected as worthy of standardization through intercalibration programmes. For example, it is likely that a gas chromatographic and/or mass spectrometric method will be required to provide chromatograms of specific hydrocarbons to determine the extent and sources of petroleum spills.

4.1 Surface sampling

The ability of sea slicks and oil films to acquire and concentrate organic pollutants has been discussed (Seba and Corcoran, 1969). To assess the extent of this effect there is a great need for nonselective techniques for sampling thin organic films at the air-sea interface. Existing techniques, which have been used by a number of investigators, include a rotating-drum surface skimmer (Harvey, 1966) which samples the upper 60 micrometres of the sea, and a screen-sampling method (Garrett, 1965) which removes a surface layer 150 micrometres thick. The rotating-drum method is somewhat expensive and mechanically complicated for routine studies in rough water and possesses a possible disadvantage of selective adsorption by different chemical classes onto the ceramic-coated cylinder. On the other hand, the screen method is almost the ultimate in simplicity. Its chief drawback is that it may be contaminated by contact with unwanted objects such as sea weed, jelly fish or other organic-containing flotsam during the time when the screen is submerged below the water surface. The screen method has been shown to be nonselective since it removes intact portions of the water surface between the wire mesh. This method could also be readily utilized for the collection of petroleum spills for thickness determination or other analyses. Surface collection techniques will be essential for the sampling and concentration of thin petroleum films and lipophilic organic pollutants associated with surface microlayers.

5. IDENTIFICATION OF RESEARCH ACTIVITIES TO IMPROVE AND DEVELOP ANALYTICAL TECHNIQUES

Expanding interest in trace organics in the ocean are due primarily to an increased demand for knowledge concerning interference with marine life. For example, one of the dangers associated with organic pollutants is that they could alter the normal pattern of natural organic compounds and thus interfere with the chemoreception by which organisms may either orient themselves or search for food. It can also disturb the pattern of pheromones during the mating season. New synthetic organic compounds manifest detectable effects at much lower levels of concentration than was previously believed. Thus, there is an obvious demand for general improvement of analytical techniques. Some of the specific improvements which are required are listed below:

a) Development and standardization of special equipment to provide valid sampling of sea water. This will include sea surface sampling apparatus and deep water samplers which do not contaminate the collected water with any organic materials or selectively remove surface active species by adsorption on the sampler walls.

b) Sampling methods to differentiate distinctly between different phases within marine samples, e.g., effect separation of the sea water, particulate matter, petroleum contaminants, etc.

c) Management of cooperative large scale analytical programmes in conjunction with environmental monitoring.

d) Develop analytical methodology which is designed to examine the chemical and biological degradation of known organic pollutants; "total fate studies".

e) Methods to isolate hydrophilic organic compounds from sea water; in addition to those of low molecular weight.

f) Estimation of previously unknown organic compounds which occur naturally in sea water at trace levels.

g) Improved methods of chemical identification of pollutants found in the ocean at ppm to ppb levels.

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Panel 5: NUTRIENT CHEMICALS

(including those derived from detergents and agricultural chemicals)

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1. INTRODUCTION

1.1 Nutrients

Nutrients to be considered in this report are those forms of nitrogen, phosphorus and silicon which are necessary to the growth of marine plants and to phytoplankton in particular. These are nitrate, nitrite, ammonia, orthophosphate and orthosilicate, together with biologically derived organic nitrogen and phosphorus compounds which can be used after microbiological breakdown. Other forms of phosphorus and nitrogen such as the polyphosphates and nitrilo-triacetic acid occurring in detergents must also be considered. All these species are of importance because of their role in eutrophication which produce far-reaching effects in the biogeochemical cycle. The influence of nutrients in this context is restricted to coastal waters, estuaries, and semi-enclosed sea areas, such as the Baltic Sea, fjords, lagoons and archipelagos, and is unlikely ever to extend to the open ocean. Nutrients should not be considered in isolation since other limiting factors, for example, bioactive trace metals, organic growth-limiting and growth-promoting substances, and the penetration of solar radiation are also important in controlling plant growth. Probably measurements of primary production (e.g., by the carbon-14 method) provide the best indication of the occurrence of eutrophication since they take account of the combined effects of all the various growth-promoting and inhibiting factors. It is because of its secondary effects that eutrophication may be so harmful. Oxygen is initially over-produced, but when the organisms die it is rapidly removed from the water, leading in extreme cases to its total depletion; this may often be followed by the formation of hydrogen sulphide. Because of the consequent changes in the carbon dioxide concentration the pH first rises and then falls drastically. Since a knowledge of pH and the concentrations of oxygen, hydrogen sulphide and total carbon dioxide can provide semi-quantitative information about the extent of eutrophication their measurement has also been considered in the present report.

1.2 Disposition of nutrients in the marine environment

The sources of nutrients and potential nutrients likely to cause eutrophication are domestic sewage, industrial wastes, and run-off and sewage from agriculture. These pollutants, in both dissolved and particulate forms, are discharged into rivers or directly in the sea, sometimes after treatment, which generally only slightly reduces the nutrient load. Little quantitative information is available for the total global discharge of nutrients. However, crude estimates of the phosphorus discharge are available for a few areas, e.g., the Baltic and the North Sea (ICES, 1969 and 1970).

1.3 Production of other wastes

Gaseous nitrogen compounds (e.g., NO_2 and NH_3) produced industrially, or by combustion, and amounting to about 50×10^6 tons/year, are probably deposited on a worldwide basis, via precipitation, and are unlikely to contribute significantly to eutrophication. The same is also certainly true for phosphorus.

1.4 Monitoring systems

Outside Europe and North America most of the major rivers do not have an effective monitoring network. Even in countries having such systems most of the emphasis is on those factors essential to water management (e.g. B.O.D. and *E. coli* counts) and little attention is paid to the total nutrient load (including potential nutrient). In only a few countries

(for example, the Scandinavian countries) is adequate monitoring carried out for those parameters which may give rise to eutrophication. It is thought that many of the existing monitoring systems could be adapted without much difficulty to obtain the essential data. In studying and controlling eutrophication in the marine environment monitoring should obviously not be confined solely to the rivers and points of direct discharge but must also be carried out on a regular and systematic basis in the estuaries and other relevant areas. The data thus obtained should be made available on an international basis.

2. EXISTING METHODS FOR THE DETERMINATION OF NUTRIENTS AND RELATED COMPOUNDS

Before discussing the determination of nutrients it is essential to consider the collection, storage and pretreatment of samples, since disregard of these crucial stages is a frequent cause of unreliable analyses.

2.1 Collection of samples

The sampling stations and grid must be carefully chosen to give a truly representative picture of the distribution of the parameters to be studied. Such a choice can only be made after a careful assessment of all the hydrographic, meteorological and other factors. Timing of sampling must be adjusted to take account of seasonal effects. In order to minimize contamination, or loss, only samplers constructed of suitable plastic materials should be used. The sub-sampling routine must be well designed and strictly adhered to in order to minimize bias.

2.2 Storage

Although it is obviously desirable to carry out the analysis immediately after collection (and indeed it is essential to do this for oxygen, hydrogen sulphide and pH measurements) it will frequently be necessary to store samples before processing. When nutrient analysis can be commenced within a few hours no difficulties arise if the samples are placed in suitable containers and kept cool in the dark. There is a considerable difference of opinion about the validity of long-term storage methods and the panel recommends that further research should be carried out before any firm recommendation can be made. However, samples for total nitrogen and total phosphorus can easily be preserved using chloroform or sulphuric acid.

2.3 Filtration

It is essential to filter samples which are turbid (this is usually the case in coastal waters). It is recommended that the filtration should be carried out through washed glass fibre or membrane filters using pressure rather than suction. It should be pointed out that filtration may cause destruction of cells and liberation of cellular fluids.

2.4 Analysis

2.4.1 Nutrients

2.4.1.1 Recommended methods and their criteria

The ideal analytical method for the determination of a nutrient should fulfil the following criteria. It should have adequate sensitivity and specificity and be sufficiently rapid. It should cover a wide range of concentrations and be useful over the whole range of salinities encountered in estuaries and the seas. It should require only readily available instruments. It should be relatively insensitive to slight variations in the reagent composition or the laboratory temperature.

Only a limited number of techniques have been applied to the determination of nutrients, most of these are spectrophotometric. Numerous modifications of these methods are in use in various laboratories. On the basis of personal experience and knowledge of the regional intercalibration experiments (Unesco, 1965 and 1968; Nordforsk, 1970) the Panel believes that manual nutrient analysis methods can be divided into two groups, those for which acceptable procedures are available, and those on which further research and intercalibration work is required. To the first category belong nitrite, phosphate, total phosphorus and ammonia (NH_3+NH_4^+). The second category comprises nitrate, total nitrogen, and silicate. The chemistry of these procedures, their sensitivities and the normal ranges of these components in unpolluted oceanic waters are shown in Tables I and II together with maximum values for highly eutrophic waters away from sewage outfalls and excluding rivers. Before these methods can be firmly recommended extensive evaluation and intercalibration studies are required. For orthophosphate, nitrite, nitrate and silicate this essential preliminary work has already been carried out during the ICES-SCOR intercalibration exercise. However, the complete evaluation of the results obtained will not be available before the Council Meeting of ICES in September-October 1971.

2.4.1.2 Alternative methods

Other methods of nutrient analysis which were considered by the Panel are given in Table III. Most of these cannot be recommended.

2.4.1.3 Design of intercalibration tests

Intercalibration exercises can only be carried out on a worldwide basis if standard samples are made available containing accurately known and realistic concentrations of the desired components, in a medium similar to sea water. These standards must be stable for several years. In this connexion the Panel wishes to draw attention to the detailed work on this subject carried out at the Sagami Research Centre under the direction of Professor K. Sugawara (Unesco, 1969); the components which he considered were phosphate, nitrate, nitrite and silicate. It would obviously be desirable to extend this list to cover ammonia and total nitrogen and phosphorus. However, in view of our general ignorance of the nature of the dissolved organic nitrogen, and phosphorus species present in the sea, the Panel does not consider that it is at present possible to prepare realistic standards for these components. Intercalibration can therefore only be carried out with natural sea water and the results obtained will give an indication only of precision and intercomparabilities of methods.

2.4.1.4 Automation of techniques

For a worthwhile study of conditions which may lead to eutrophication an intensive sampling programme is necessary and the analysis of the great numbers of samples involved is a serious problem. The burden on the analyst can be most readily eased by adoption of one of the automatic analysers which are now becoming available. Such instruments have the advantage that they require only very small samples and they can readily be used for continuous analysis and for profiling. The raw data obtained from such instruments can be readily stored and processed by computers. The instruments are of two types, batch analysers and continuous flow analysers. Although the former may be considerably faster, in operation they have the disadvantage that they cannot be used for simultaneous analysis of a number of components, or for continuous analysis. In principle, any manual method of photometric analysis can be readily adapted to these systems, and in fact many of the methods referred to in Tables I and II have been very successfully adapted for use on the Technicon Autoanalyser. Some of the automated techniques (e.g. for PO_4^{3-}, SiO_4^{4-}, NO_2^- and NO_3^-) have been the subject of intercalibration studies, which have shown that their accuracy and precision are equal to that of the normal methods. During work at sea the precision generally exceeds that of the manual methods.

2.4.2 Related parameters

2.4.2.1 Oxygen

For all but the most polluted waters the determination of oxygen is most accurately carried out by modifications of the Winkler Method as described by Carpenter (1965) and Grasshoff (1962). The thiosulphate solution must be standardized against potassium iodate or bi-iodate. These methods have been the subject of recent intercalibration studies. It should be stressed that since incorrect sampling is one of the principal sources of error in the estimation of oxygen, great care should be taken at this stage. It is particularly recommended that the whole sample should be used in the titration.

Electrometric methods for the determination of oxygen are useful for profiling and for examinations of highly polluted waters, but the variability of the indicator electrode makes it essential to calibrate the system frequently.

2.4.2.2 Hydrogen sulphide

Sampling for hydrogen sulphide must be carried out with the same care as for oxygen. The methylene blue method (Fonselius, 1962) provides a sensitive and reliable technique for its determination in the range 0-50 μg-at H_2S-S/l. The determination of the sulphide in the working standard must be carried out by the iodine method. The estimation of higher concentrations can be performed either by the iodine method (Johnson et al., 1964) or by diluting the sample after fixation of the sulphide as colloidal cadmium sulphide and then determining as methylene blue. The sulphide-electrode system may be of some value for monitoring purposes, but the Panel doubts the reliability of the currently available electrodes.

2.4.2.3 Total carbon dioxide

Considerable inaccuracy results if the equations of Buch (1951) or Lyman (1956) are used to calculate the total carbon dioxide concentration in eutrophic waters because of the effect of weak acids other than H_2CO_3 or H_3BO_3 on the alkalinity. In such waters, especially, it is necessary to determine total carbon dioxide directly, preferably by infra-red techniques (Keeling, 1965).

2.4.2.4 pH

Intercalibration studies have shown that to obtain pH determinations which are comparable and reproducible to $\pm$0.01 unit necessary to make the measurements at a controlled standard temperature in a closed system. The electrode system should be standardized with the N.B.S. buffers as recommended by Gieskes (1970). Correction to in situ pH should be made according to the procedure used by Gieskes (loc. cit.).

2.4.2.5 Total organic carbon

The total organic carbon (dissolved and particulate) concentration gives valuable information about the extent to which eutrophication has occurred. Appropriate manual and automated methods are availabe for the determination of these important factors (Menzel and Vaccarro, 1964).

3. FUTURE DEVELOPMENTS

It is the feeling of the Panel that for many of the nutrient compounds the existing methods and their modifications fulfil the requirements which are outlined under 2.4.1.1. However, for some of the others the position is not so satisfactory. This is particularly the case for nitrate, total nitrogen and silicate. There is a clear case for further development work on nutrient analysis. This should include not only the evaluation of

TABLE I

Compounds for which Acceptable Methods are available

Compound	1) Sensitivity (routine method) $\frac{\mu g\text{-at}}{dm^3}$	Normal range in a) surface b) deep water $\frac{\mu g\text{-at}}{dm^3}$	2) Maximum range under unusual conditions	Chemistry involved	Ref.
PO_4^{3-}-P	±0.02	a) 0 - 1 b) <3	10	Formation of heteropoly acid, reduction of the heteropoly acid by ascorbic acid	Murphy and Riley, 1962 Koroleff, 1970a
NO_2^--N	±0.02	a) 0 - 1 b) <3	5	Formation of azo dye	Bendschneider and Robinson, 1952
Total P	±0.03	a) 0 - 1 b) <3	15	Pressure digestion with potassium persulphate acid digestion with perchloric nitric acid U.V. irradiation all followed by determination of PO_4^{3-}	Koroleff, 1970a Burton and Riley, 1956 Armstrong and Tibbitts, 1968
NH_3+(NH_4^+)-N	±0.05	a) 0 - 3 b) 0 - 3	20	Indophenol blue formation with sodium nitroprusside as catalyst	Koroleff, 1970b

1) Sensitivity = 2 x standard deviation of the blank

2) Not in the vicinity of outfalls or in rivers

TABLE II

Component for which the Existing Methods must be considered Tentative

Compound	Sensitivity [1] (routine method) $\frac{\mu g\text{-at}}{dm^3}$	Normal range in a) surface b) deep water $\frac{\mu g\text{-at}}{dm^3}$	Maximum range [2] under unusual conditions	Chemistry involved	Ref.
NO_3^--N	0.05	a) 0 - 5 b) < 40	40	Heterogenous reduction to NO_2^- by amalgamated or copperized cadmium followed by azo dye formation	Morris and Kiley, 1963 Grasshoff, 1964b Strickland and Parsons, 1968.
Total N	0.1	a) 5 -50 b) > 40	80	Persulphate or UV digestion followed by nitrate determination	Koroleff, 1969 Armstrong, 1963
H_4SiO_4	0.5	a) 0 -20 b) > 200	-	Formation of silicomolybdic acid	Grasshoff, 1964a Unesco, 1969
	0.05		-	Formation of silicomolybdic acid followed by reduction to molybdenum blue	Mullin and Riley, 1955a
Poly-phosphates	0.04	0	?	Acid hydrolysis followed by determination of liberated orthophosphate (no preservation possible)	Armstrong and Tibbitts, 1968

1) Sensitivity = 2 x standard deviation of the blank
2) Not in the vicinity of outfalls or in rivers

TABLE III

Alternative Methods considered by the Panel

Compound	Method	Ref.
PO_4^{3-} -P	1) Formation of phosphomolybdic acid followed by reduction with stannous chloride	Harvey, 1948 Unesco, 1969
	2) Formation of phosphomolybdic acid followed by extraction and determination of the molybdenum by atomic absorption or spectrophotometry	Sugawara and Kanamori, 1961 Hurford and Boltz, 1968
NO_2^--N	Diazotization of sulphanilic acid followed by coupling with ∝-naphthylamine	Rider and Mellon, 1946
Total P	Digestion with hydrogen peroxide and sulphuric acid	Redfield et al., 1937 Burton and Riley, 1956
(NH_3+NH_4) -N	1) Nesslerization	Buch, 1915
	2) Bordeaux-B method	Koroleff, 1966
	3) Distillation followed by indophenol blue formation	Riley, 1953
	4) Rubazoic acid methods	Johnston, 1966
	5) Oxidation to nitrite	Richards and Kletsch, 1964
	6) Trichloramine formation	Newell, 1967
NO_3^--N	a) Photometric with 1) Diphenylbenzidine	Atkins, 1954
	2) Strychnidine	Harvey, 1926
	3) Diphenylamine	Isaeva, 1956
	4) Nitrosyl chloride	Armstrong, 1963
	5) Homogenous reduction with hydrazine	Mullin and Riley, 1955b
	b) Polarographic reduction	Chow and Robinson, 1953
Total N	Kjeldahl method preceded by reduction	Strickland and Parsons, 1968

modifications of existing procedures but also the search for new and more accurate, sensitive and specific techniques. The rapid development of new instrumentation and reagents makes it extremely important to maintain a dynamic outlook in this field. Any new techniques must of course be carefully investigated before adoption. It is essential that they should also be compared with existing established procedures in order to maintain continuity. It is desirable that the task of devising and evaluating new methods should be assigned to particular research institutes and that funds should be allocated from national and international sources for this work. A handbook should be prepared giving all essential details of recommended methods of analysis for nutrients, and their related compounds and for determining primary production in polluted and unpolluted waters.

In order to understand the dynamic processes occurring in estuaries and coastal waters, there must be close cooperation of limnologists and marine scientists. This is especially true for the establishment of successful monitoring systems.

Sediments often play an important part in the nutrient balance in eutrophic waters since they act as reservoirs from which nutrients and potential nutrients may be regenerated under suitable conditions. The panel is of the opinion that it would be of considerable value to have reliable methods for nutrient element determination in near-shore sediments and recommends further investigation of the problem.

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Panel 6: SUSPENDED SOLIDS AND TURBIDITY

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1. INTRODUCTION

1.1 Suspended solids

Natural suspended matter in the sea consists of a large number of components: inorganic materials (sand, clays and minerals), living organisms (phytoplankton, zooplankton, bacteria, yeasts and fungi), and organic detritus. Frequently suspended particles are conglomerates containing various components. Sizes vary from less than one micron up to several millimetres; the majority by number of the particles in the open sea have sizes less than 10 μ. In coastal areas with strong tidal streams coarse sand grains may be carried in suspension. Concentrations of suspended matter vary from less than 0.1 mg/l in the open oceans to many grams per litre in estuaries and nearshore waters.

1.2 Turbidity

Turbidity in the sea is a general term indicating the optical state of the water. Most often turbidity is estimated by visual observation of light upwelling from the sea. In a strict sense the degree of turbidity may be expressed in terms of light attenuation coefficient, c (formerly called extinction coefficient). This is defined by the relation:

$$F = F_o e^{-cr}$$

where F_o is the incident flux and F the flux transmitted through the pathlength r.

1.3 Solid pollutants

Suspended pollutants consist of domestic sewage and waste products from industries. A reliable distinction between waste products and natural materials in turbid waters is only possible if the pollutants have specific characteristics. In normally clear sea water the presence of large quantities of solids may in itself indicate a source of pollution.

1.4 Transport paths

Most of the natural inorganic solid matter is carried to the sea by rivers; in comparison, the amounts of inorganic waste are small. Suspended organic waste, on the contrary, often dominates over natural organic matter in rivers. During river transport bacteriological changes are small in cases where the residence time of the water is short. Most of the breakdown processes then take place in the estuaries or in the sea nearshore. Part of the inorganic matter, specifically clays, flocculates in the brackish water zone, causing an increase in particle size from, for example, one to ten μ. In polluted rivers sufficient electrolytes are often present to complete flocculation before the water reaches the estuarine zone. Part of the organic matter may also flocculate, including certain types of colloidal and dissolved organic matter. Inorganic and organic matter (living or dead) adsorb and thus concentrate a wide range of dissolved pollutants, including heavy metals and pesticides.

Particulate substances are deposited in estuaries and carried away by currents, depending on particle size and the current régime. In tidal areas large amounts of material are stirred up and redeposited every tidal cycle. Dispersal away from the coasts is often seriously restricted by various types or sediment traps. For example, only a very small part of the solid matter carried into the North Sea leaves the area. Frequently suspended matter discharged into the sea returns to neighbouring shores.

In addition to river transport, rapidly growing amounts of solid wastes are brought into the sea by pipelines or dumped from barges. For example, the amount dumped near New York represents the largest source of sediments entering the Atlantic Ocean from the North American Continent (Gross, 1970). The effect on the sea of pipelines differs from that of rivers in that the residence time of materials in the pipes is even shorter, so that practically no decomposition takes place before the materials reach the sea. However, pipelines can be connected with purification plants.

Very fine-grained materials are carried away into the open sea and will slowly settle into deeper waters. Discontinuity layers may retard further sinking, so that particles are again concentrated there.

1.5 Effects of pollutants

1.5.1 Oxygen consumption

A heavy load of suspended organic matter, together with dissolved organic substances, will seriously deplete the amount of available oxygen at depth.

1.5.2 Influence on productivity

Solid inorganic pollutants will hamper light penetration into the sea and may reduce primary production per unit area. Organic pollutants, on the other hand, will enrich the sea with nutrients, which may cause a local increase in productivity.

1.5.3 Influence on the sea floor

Inorganic waste deposits may modify the structure of the sea bottom; organic waste may cause anaerobic conditions and formation of hydrogen sulphates in or near the bottom. In both cases the composition of benthic communities will be changed and generally be impoverished. Sediment feeders and filtering organisms may incorporate solid waste and thus become toxic.

2. METHODS FOR DETERMINING SOLIDS

The principal difficulty in studying the distribution and nature of suspended matter in the sea water is to obtain methods for its quantitative determination and further to differentiate between the living and dead components (Parsons, 1963). There has been no method developed yet to determine only the particles which are introduced by pollution.

2.1 Total particulate matter (seston)

The total particulate matter in sea water can be determined by filtering a known volume of sea water through pre-weighed filters. The particulate matter can then be estimated as the increase in weight on the filter. It is important for this estimation to use filters with defined pore sizes and known filtering characteristics, e.g., membrane filters of a pore diameter of 0.45 μ or 0.7 μ. The suction pressure should not exceed 1/3 atm. to prevent loss in weight during filtration. The filters should be rinsed twice in 10 ml of distilled water to remove salt water. After drying the filters at 75°C for one hour they have to be weighed again. Banse et al. (1963) introduced a weighing technique to overcome the electrostatic charges on the membrane filters. Control filters should be used to eliminate errors due to humidity. The main disadvantage of this gravimetric technique is that it cannot be used aboard a ship.

2.2 Size

The size distribution and nature of suspended solids can be obtained by using microscopic methods. The enumeration of phytoplankton abundance provides an important and frequently indispensable measure of the success, growth and stage of succession of a species or community.

There is no ideal method of enumerating phytoplankton but several methods are available, each having advantages and disadvantages.

Quantitative enumeration and identification of phytoplankton can be carried out using settling chambers (Utermöhl, 1958), counting chambers (Sedgwick - Rafter chambers or modifications, Jackson and Williams, 1962), or membrane filter techniques (Holmes, 1962).

A method of particular value in identifying the proportion of a plankton population containing photosynthetic pigments, the fluorescent microscopy method (Wood, 1962), can be used with living cells or with those that have been preserved in glutaraldehyde and refrigerated for not more than a week.

Particle counts from unconcentrated water samples are best carried out with the Utermöhl technique. The preserved particles settle to the bottom of special settling chambers, and are then counted and identified from beneath the chambers by using an inverted microscope. Before the settling of the organisms in the sedimentation tubes, stain (e.g., Rose Bengal) can be added to facilitate the distinction between living and dead particles. Different sizes of chamber and several magnifications up to 500 times should be used to get significant counts on most organisms and dead particles. The microscopic methods have the advantage of qualitative and quantitative counts of the total particulate matters. Their disadvantage is that this method is rather time consuming.

Microphotographs of particles on the bottom of the settling chamber can be counted with a particle size analyser which determines simultaneously the diameter of individual particles and their numbers (Krey, 1961; Lenz, 1968).

The settling of particles by gravity is also used for the estimation of particle size distribution using equations for the settling velocity. This technique is mainly used in geological work for inorganic matter, e.g., the pipette method and the sedimentation balance.

Non-concentrated or, in the case of large particles, concentrated samples of sea water can be analysed by means of an electronic particle counter. This instrument was developed by Coulter (U.S. patent No. 2 656 508) to count and size erythrocytes. A glass tube attached to the instrument is dipped into the sample. At the base of the tube is a tiny hole of a given diameter. At both sides of this orifice an electrode is situated.

Measured volumes of the sample are sucked through the hole, and whenever a particle passes, the electrical field maintained between the electrodes changes, since the resistivity of the particle is different from that of the electrolyte. These changes are displayed on an oscilloscope, the height of the peaks being proportional to the volume of the particles. Particles of a size range 1 to 1 000 microns can be counted and sized, giving a size-frequency distribution of the suspension in the sample. Sheldon and Parsons (1967) give a detailed procedure on the use of the Coulter Counter in marine science.

2.3 Living and dead matter

The distinction between the living and dead organic particles can be obtained in subtracting the "living" fraction from the total. The living part can be determined by various chemical analysis like organic particulate carbon, chlorophyll, protein, ATP, DNA, etc., or by converting the plankton counts to organic matter. These estimates are only an

approximation because conversion factors have to be used to calculate the living portion (Hagmeier, 1961; Holm-Hansen et al., 1965; Larrance and Kovala, 1966; Strathmann, 1967; SCOR-Unesco Working Group 17, 1966; Strickland and Parsons, 1968).

3. TURBIDITY

3.1 Substances absorbing and scattering light

Light attenuation in the sea is caused by the water itself, by suspended particles and by dissolved substances (Jerlov, 1968). Pure water is most transparent in the blue; red light is strongly absorbed. Particles are responsible for light absorption as well as scattering. On an average, particle absorption is found to be stronger in the shortwave part than in the longwave part of the spectrum whereas particle scattering usually is little dependent on wavelength. The sea salts exert only a weak influence on the absorption. Among the optically active dissolved substances some soluble humus-like substances known under the collective name of "Gelbstoff" exhibit absorption which starts in the yellow and grows strongly toward shorter wavelengths. Gelbstoff is formed from carbohydrates in the presence of amino acids. The end product is chiefly melanoidines with a by-product fluorescing at 490 nm. Large quantities of humus compounds are brought to the sea by rivers, especially at high northern latitudes, but Gelbstoff is also of immediate marine origin.

The general background created by particles and Gelbstoff makes it difficult to distinguish the optical effect of any particulate or dissolved pollutant.

3.2 Optical methods

Current methods for observing turbidity are surveyed below. The optical meters are sensitive enough to detect small changes in the concentrations of suspended matter and coloured dissolved substances. The methods can be relatively quickly performed. At the present stage of technical development they do not differentiate between organic and inorganic matter. The exposé below is presented with a view to judging the usefulness of the methods for pollution research.

3.2.1 Secchi disc

This well known method yields a rough measure of the average turbidity from the surface down to the depth where the contrast between the disc and the background vanishes. Several attempts have been made to relate the Secchi disc depth to the light attenuation coefficient. It is evident that the observation is subjective in its approach and to some degree dependent on the lighting conditions above the sea. Shallow waters of a depth similar to the Secchi disc depth are not accessible for observation. In spite of these shortcomings the method keeps its usefulness because of its simplicity (Tyler, 1968).

3.2.2 Beam transmittance meter (transmissometer, transparency meter)

The simple principle of this meter is to produce a parallel beam of light which, after passing a geometric light path of fixed length, impinges upon a detector, usually a photovoltaic cell. In turbid water a path length of one metre or even less is sufficient. Joseph (1949) has described a prototype which is little affected by ambient natural light in the sea.

The transmittance meter is designed for measuring the attenuation coefficient defined as the sum of the absorption coefficient and the scattering coefficient. The advantage of this in situ meter (provided with a depth-sensing unit) is that a defined attenuation recorded as a function of depth reveals the vertical structure of the distribution of this parameter; for instance particle accumulations are often present near bottom or associated with a discontinuity layer in the sea. Measurements for different colours may serve to characterize pollutants and trace their

spreading. The transmittance meter can be designed for long-time recording. Towed instruments may be used to increase the coverage of the methods.

3.2.3 Scattering meter

The scattering meter aims at a direct determination of the particle component. Measurements involve irradiating a sample volume and recording, generally using a photomultiplier tube, the light scattered by the volume through various angles. Several types of *in situ* and *in vitro* instruments have been developed (Jerlov, 1968). A fixed angle of 45° is often chosen since 45° scattering is proportional to the total scattering over all angles. The latter can also be obtained by integrating meters. In laboratory instruments it is obligatory to agitate the samples in the water bottle and in the scattering cell in order to secure a homogeneous sample and prevent settling of large or heavy particles. The *in situ* method is definitely to be preferred, especially as it allows for finding details in the vertical particle structure.

The obtained scattering values represent approximately the total surface of the various kinds and sizes of particles. In ocean water the wavelength dependence of scattering is not important. Pollutants containing coloured particles may, however, impose a spectral change on scattering.

The best adaption to routine observations is displayed by an *in situ* meter of the integrating type. A sketch of such an instrument is shown in the figure. The light source L is an incandescent lamp (30 W) together with an opal glass in contact with the water. The receiver O contains a detector, for instance a photodiode, in combination with a lens-pinhole system. With a lens focal distance of 50 mm and a pinhole diameter of 2 mm the system restricts the acceptance semi-angle to about 1°. The length of the detectivity beam is limited by a light trap T facing the receiver.

The geometry of the meter is adapted so as to minimize the distance between the opal glass and the detectivity beam. If the opal glass is a cosine emitter the detector will receive light scattered from particles nearly over the whole scattering range 0 to 180°; the theory shows that for constant emission of the light source the measured radiance is proportional to the total scattering coefficient with an accuracy sufficient for all practical purposes. Because of the small dimensions of the instrument the attenuation of light in the pathway is insignificant (if the water is not too turbid) and can be taken into account when the meter is calibrated.

The function of the meter may be affected by ambient daylight in the uppermost stratum of the sea. A red filter (Schott RG610, 2 mm) in front of the detector largely reduces this effect. A screening from daylight may be useful but must not obstruct the free water circulation through the scattering volume.

The meter is preferably provided with a depth sensing unit so that records of scattering can be obtained as a function of depth by means of an x - y recorder.

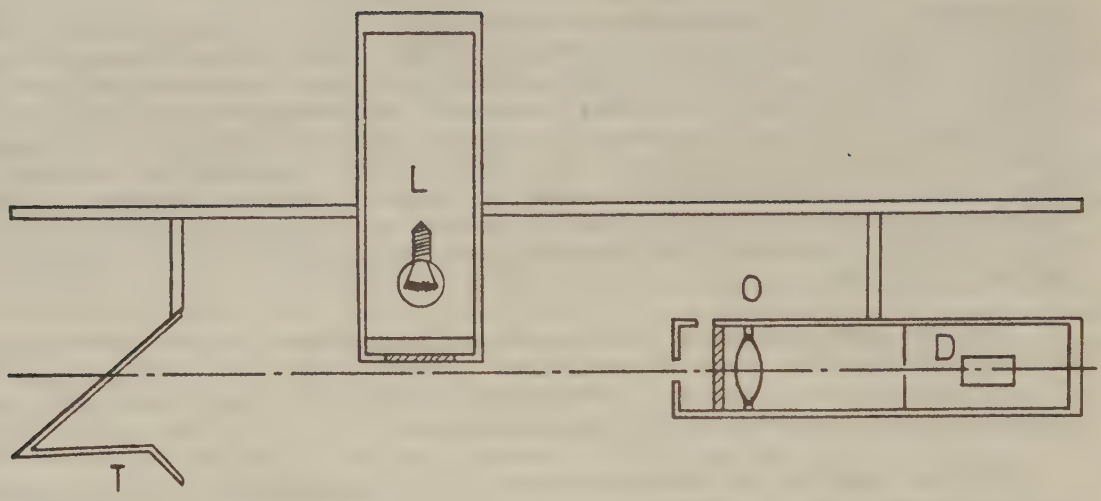

Figure 1: Scattering meter

3.2.4 Colour of the sea

The colour of the sea viewed from a point just above the surface is determined by the spectral composition of light back-scattered from subsurface levels and of light reflected from the sea surface. The oceanographic concept of colour refers adequately to colour in situ which does not involve reflected light. On account of selective absorption by particles and Gelbstoff, the colour is gradually changed with increasing turbidity from the deep blue in the clearest ocean waters, over green to brown in the most turbid waters, for instance the Baltic. The red back-scattering is extremely low in clear waters and grows with increasing turbidity.

The conventional three colour system can be substituted for a colour system with two components only. A spectral range in the blue (450 nm) and another in the green (525 nm) may be utilized to represent colour and ultimately the optical properties of a water mass. The ratio green/blue for the sea is a sensitive indicator of colour changes due to the selective effect of suspended and dissolved matter.

3.2.5 Remote measurement of the colour of the sea

The rapid development of oceanographic exploration from the air also involves pollution research. By means of a spectrophotometer on a platform in aircraft (or spacecraft) the upwelling light from the sea, which determines the colour, is analysed and compared with the incident light from the sun and sky. Changes in the spectra due to pollutants are thus revealed in space and time.

The upwelling light received by the photometer includes light scattered back from the sea, which is the requested component for observation, but also reflected light from the surface and "air light", i.e., light scattered by the air and by particles in the air. Reflected light and air light appear as noise interfering with the signals. The disturbing effect of reflection can be reduced. Thus Clarke et al. (1970) who measured chlorophyll concentration as indicated by ocean colour, placed a polarizing filter oriented at right angles to the major axis of polarization of the reflected light, over the receiving aperture of the spectrophotometer and tilted the instrument at 53° from the vertical (the Brewster angle) away from the sun.

Air light recorded from aircraft increases considerably with altitude and is also as mentioned dependent on air turbidity. Since it is mostly a Rayleigh scattering, air light displays a continuous increase toward short wavelengths whereas the upward light in the sea shows a definite maximum; the spectral distribution of upward light is peaked at 450 nm in clear ocean water and shifts toward long wavelengths with increasing turbidity.

The briefly outlined remote measurements of colour makes mapping of oceanic areas possible in favourable weather, with a coverage not obtainable from shipboard observations. Computers can be utilized to generate the map of pollution (White, 1970). The information gathered is, however, limited to the uppermost layer of the sea and the significant vertical structure of the distribution of pollutants is not revealed.

3.2.6. Fluorescence

Fluorescence from organic substances can be studied on collected water samples by means of a laboratory meter. Pumping of water from different levels in the sea increases the efficiency of the laboratory method. Since various organic pollutants are likely to fluoresce in different parts of the spectrum, fluorescence can be employed as a possible indicator for mapping the distribution of such pollutants.

Recently an in situ fluorimeter has been designed (Kullenberg and Nygård, 1971) which fulfils the demand of having requisite sensitivity and yielding quick and reproducible records as a function of depth. This has so far been fitted to detect only the fluorescence at 490 nm mentioned, but the meter can easily be adapted for other fluorescent ranges. It seems interesting to test the value of this indicator for tracing pollutants.

4. CONCLUSION

It should be pointed out that the optical meters yield results which are often expressed as attenuation or scattering coefficients. The detection of pollutants and the study of their horizontal and vertical spreading in the sea do not require calibration in absolute units. At present it is not possible to suggest simple means to arrive at primary or secondary standards.

It is clear from the description of methods that their potential role for assessment of water pollution largely depends on defining or classifying different types of pollutants. In other words the detection of pollutants would involve an identification of the substances by their physical and chemical nature and, as regards optical methods, by their spectral absorption and emission. Our present knowledge about these parameters is restricted. The adaption of the methods to the character of existing pollutants would greatly improve their usefulness. It is urgent that further research pays attention to this problem.

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Panel 7: RADIOACTIVITY

A. Preston (Chairman)
R. Fukai
H.L. Volchok
N. Yamagata

1. INTRODUCTION

Man has been increasing natural background radiation by the addition of artificial (man-made) radioactivity throughout this century. In recent decades artificial radioactivity, radioactive isotopes produced principally by nuclear fission and nuclear activation, have entered the environment, including the oceans, largely from nuclear explosions and from the generation of electrical power from nuclear fission. Other contributory sources have included maritime nuclear propulsion, isotope power sources, loss of nuclear weapons and the medical and research uses of radioisotopes.

However, over the past years the highly toxic nature of these materials has ensured that, except in the context of the loss or testing of nuclear weapons, the amounts introduced have been strictly limited under national regulations based on internationally promulgated standards for the safe exposure of human populations to ionizing radiation (ICRP, 1966). It is well established that the radioactive contamination problem is primarily one of public health and that the maintenance of proper public health standards will ensure more than adequate standards for the protection of marine organisms (IAEA, in press; Templeton et al., in press).

The continuing review of data on the biological effects of ionizing radiation under the auspices of UNSCEAR and the recommended standards of exposure (dose-limits) based on it by ICRP have provided a very firm and perhaps unique base from which to proceed to the assessment of environmental problems and the design and implementation of proper control procedures. In a marine context the IAEA report "Radioactive Waste Disposal into the Sea" (IAEA, 1961) was the first report to give international guidance for the controlled disposal of a waste material to the sea. This report has recently been reviewed (IAEA, in press) and endorsed as a valid approach to the sea disposal of radioactive waste and further recommendations have been made to the IAEA for the preparation of a technical report which will provide a complete manual of procedures for applying the principles it sets forth.

2. RATES OF INTRODUCTION

The data in Table I indicate the order of magnitude of the total artificial radioactivity content of the world oceans in 1970 contributed by weapon test fallout and controlled radioactive waste disposal, since other sources are negligible by comparison. This figure, 10^9 curies, may be compared with the 5.10^{11} curies of natural ^{40}K in the oceans indicating that artificial radioactivity is approximately 1/1 000 of the total natural radioactivity in the oceans, but this simple comparison should not be taken as indicating the relative biological significance of the different materials. The artificial radionuclides have very widely ranging toxicities and their significance in a given environment will depend not only on this but also the uses of that environment which will lead to human radiation exposure.

The second column of the Table indicates the situation that may exist at the end of the century assuming the present level of nuclear weapon testing and disposals of low level radioactive waste in proportion to the growth in nuclear power. In fact trends over the last decade show that improvements in waste management have achieved a reduction in the amount of radioactive material which reaches the marine environment per unit of fuel reprocessed. So that there is every expectancy that a lower inventory may be achieved.

TABLE I

Total Content of Artificial Radionuclides in the World Ocean

	Year 1970	Year 2000
Nuclear Explosions		
Fission Products (exclusive of Tritium)	2-6 x 10^8Ci	? x 10^8Ci 1/
Tritium	10^9Ci	? x 10^9Ci 1/
Reactors and Reprocessing of Fuel		
Fission and Activation Products (exclusive of Tritium)	3 x 10^5Ci	3 x 10^7Ci
Tritium	3 x 10^5Ci	? x 10^8Ci
Total	10^9Ci	10^9Ci

1/ Assumed that atmospheric nuclear testing will continue at about the rate of 1968-1970

Concern has been expressed in recent years over problems relating to noble gasses, principally ^{85}Kr; and to tritium. The cumulative world total of ^{85}Kr by the end of the century will approximate 10^{10} curies (SCEP, 1970) distributed throughout the atmosphere but with locally high concentrates in the vicinity of fuel reprocessing plants. Krypton is soluble in seawater and calculations based on the distribution of stable krypton suggest that only 0.1-0.2 per cent of the ^{85}Kr atmospheric inventory will reside in the surface 100 m's of the world ocean, 0.3-0.5 pCi/litre. As an inert gas biological involvement would be negligible and the radiation field experienced by marine organisms from such a low concentration as an external source would be trivial by comparison with that due to the naturally occurring ^{40}K (300 pCi/litre).

Tritium, which is of very low radiotoxicity, will not concentrate to any extent in biological materials and does not present a significant problem in the context of marine disposal.

Uncontrolled releases, other than the nuclear explosions discussed above, are likely to be infrequent, of small magnitude relative to the capacity of the world ocean, and to result in national, or perhaps an occasion, regional problems.

It therefore seems clear that the artificial radioactive content of the world ocean, exclusive of tritium, over the next three decades will not increase very much if at all. Certainly the more significant contribution in the future will be from nuclear power programmes and fuel reprocessing in particular, whereas the major contribution in the past has been from nuclear weapon testing. It may well be that arguments, other than those advanced on public health or resource considerations, will dictate lower rates of introduction than those envisaged so that lower overall contents will be achieved by the year 2000.

3. ENVIRONMENTAL CONCENTRATIONS

The radionuclide concentrations encountered in the principal compartments of the marine environment as a result of fallout from weapon testing and the controlled disposal of radioactive wastes are set out in Tables II and III. In general, weapon test fallout has resulted in low levels of contamination which are global in extent. Much higher levels have of course existed for short times, weeks or months, in the immediate vicinity of nuclear explosions. Waste disposal operations have on the other hand produced and maintained locally high concentrations, but never as high as those in the vicinity of nuclear explosions at short times after the explosion. The maintenance of proper public health procedures has ensured, and will continue to ensure, the acceptability of radionuclide concentrations in the vicinity of disposal areas and a fortiori exclude the possibility of significant global contamination.

TABLE II

Radionuclide Concentrations from Global Fallout (pCi/l Seawater; pCi/kg Dry Sediments; pCi/kg Wet Biological Material

Radionuclide	Water	Sediments	Biological Materials			
			Seaweeds	Molluscs	Crustaceans	Fish
^{3}H	$1 - 10^{2}$					
^{54}Mn	(1)	$10^{3} - 10^{4}$	10^{3}			
^{90}Sr	$10^{-1} - 1$	$1 - 10^{2}$	$1 - 10$	$10^{-1} - 10$	$1 - 10$	$1 - 10$
$^{95}Zr/Nb$	$10^{-1} - 10$	$10^{2} - 10^{5}$	$10^{3} - 10^{4}$			
^{106}Ru	$10^{-2} - 1$	$10^{2} - 10^{5}$	$10 - 10^{4}$	$10 - 10^{2}$	$1 - 10^{2}$	$1 - 10^{3}$
^{137}Cs	$10^{-1} - 1$	$10 - 10^{4}$	$1 - 10$	$1 - 10$	$1 - 10$	$1 - 10^{2}$
^{144}Ce	$10^{-2} - 1$	$10^{2} - 10^{5}$	$10 - 10^{4}$	$10 - 10^{3}$	$1 - 10^{2}$	$1 - 10^{2}$
^{239}Pu	$10^{-5} - 10^{-3}$	$10^{-1} - 1$	1	10^{-1}		10^{-3}

TABLE III

Radionuclide Concentrations resulting from the Controlled Disposal of Radioactive Wastes from Nuclear Power Production (pCi/l Seawater, pCi/kg Dry Sediments, pCi/kg Wet Biological Material)

Radionuclide	Water	Sediments	Seaweeds	Molluscs	Crustaceans	Fish
^{3}H	$10^{1} - 10^{3}$					
^{32}P	$1 - 10$			$10^{2} - 10^{3}$		
^{54}Mn						
^{55}Fe	$10^{-1} - 10$		10^{2}	$10^{2} - 10^{3}$		
^{60}Co	$10^{-2} - 1$	$10^{2} - 10^{3}$	$10^{2} - 10^{3}$	$10 - 10^{3}$		
^{65}Zn	$10^{-3} - 1$	10^{3}	$10^{2} - 10^{3}$	$10^{2} - 10^{5}$		
^{90}Sr	$1 - 10^{2}$		$10 - 10^{2}$	$10^{2} - 10^{3}$	10^{3}	1
$^{95}Zr/Nb$	$1 - 10^{3}$	$10^{5} - 10^{7}$	$10^{4} - 10^{6}$	$10^{4} - 10^{6}$	$10^{3} - 10^{4}$	
^{106}Ru	$1 - 10^{3}$	$10^{5} - 10^{8}$	$10^{4} - 10^{6}$	$10^{4} - 10^{6}$	$10^{3} - 10^{5}$	10^{3}
^{110m}Ag	$10^{-3} - 10^{-2}$			$10^{2} - 10^{3}$		
^{134}Cs	$1 - 10$	10^{3}				10^{3}
^{137}Cs	$1 - 10^{2}$	$10^{2} - 10^{4}$	10^{3}	$10^{2} - 10^{3}$		$10^{3} - 10^{4}$
^{144}Ce	$1 - 10^{3}$	$10^{5} - 10^{7}$	$10^{4} - 10^{6}$			
^{239}Pu		$10^{2} - 10^{5}$	$10^{2} - 10^{4}$			$1 - 10$

4. MONITORING REQUIREMENTS

Monitoring or surveillance of the marine environment is taken to mean the measurement of radionuclide concentrations or radiation for reasons related to the assessment, or control, of radiation exposure, and primarily that of man. In a contemporary context, and it is expected in the future, such exposure arising in the marine environment will result from the controlled disposal of radioactive wastes and the first stage in any monitoring operation will be to assess the quantities of radioactivity released to sea. This, in many cases, will be sufficient and monitoring of the environment will only be required where a significant fraction of the pre-operationally assessed capacity of the local environment is being utilized (Preston, in press).

In a global context this latter situation cannot arise, in the foreseeable future, under presently employed methods of control. However, it has recently been recommended to the IAEA that steps be taken to set up an international register of disposals of radioactive waste into the sea as a first stage in global monitoring. If the need for second stage surveillance arises it can best be catered for initially by an international record of environmental monitoring data provided by the various national regulatory authorities under whose control the radioactive material was originally introduced to the environment.

We recognize the contribution made by the measurement of low level radioactivity, such as that of fallout radionuclides on a global scale. Whilst not regarding this as monitoring within a control context, we consider that a useful contribution has been and will continue to be made, by such studies, to oceanic and atmospheric research.

5. DETECTION AND MEASUREMENT OF RADIONUCLIDES

The IAEA has recently published a review of the methods currently available for the detection and measurement of radionuclides in the marine environment (IAEA, 1970) and this section draws largely on the material available in that review but with the emphasis on analyses in a control context.

5.1 Required lower limits of detection

In considering a scheme of radionuclide analysis for the control of radioactivity, it is essential to have some idea of the required lower limit of detection for the radionuclides concerned. This will enable decisions on sample size and the required sensitivity of the radiometric equipment to be made. These required lower limits of detection can be derived from a general consideration of the ICRP recommendations (ICRP, 1960) and by assuming certain maximum consumption rates for important groups of marine foodstuffs. The necessary data and the results of the derivations are given in Table IV. On the basis of permissible daily intakes of individual radionuclides (members of the public, ICRP, 1960), concentration factors for individual elements in fish, seaweed and shellfish and the assumed maximum consumption rates for these materials, it is possible to compute the concentration of radionuclides in seawater in equilibrium with organisms contaminated at levels compatible with permissible ICRP values. The required lower limits of detection are defined as 1% of these concentrations. The values given in Table II for various radionuclides are in the range 0.04 to 10 pCi/litre, except for strontium-89 and ^{3}H. In deriving these values, estimates of similar lower limits of detection for marine organisms are also produced. In fact, when critical radionuclides and routes for specific radioactive waste disposal operations are known, the normal practice for controlling discharges is to measure radionuclides in the critical materials (e.g. food organisms or sediments) and not in seawater; in so doing the lower limits of detection may be raised several orders of magnitude above the values given in the Table.

5.2 General scheme

A general scheme for radionuclide analysis in a control context is given in Figure 1. For samples of seawater as well as those of bio-materials and sediments the final determination of the majority of the radionuclides concerned can be performed by gamma-spectrometry (Dutton, 1969; UKAEA, 1962). For radionuclides which do not emit gamma radiation measurement of radioactivity has to be made by beta counting, which can also be applied in some cases as an alternative to gamma-spectrometry following radiochemical separations. In some cases simple gross beta counting can afford a useful means of controlling marine radioactivity in specific situations if the composition of released effluents and the critical pathways of individual radionuclides are known. Gross beta counting of environmental samples has been discussed by Dutton (1968).

TABLE IV

Required Lower Limits of Detection in Seawater of the Principal Radionuclides Concerned in Waste Disposal Operations

Radionuclide	Permissible [a] daily intake (pCi/d)	Lower limit of detection based on consumption of [b]						Required lower limit of detection in seawater [c] (pCi/litre)
		Fish (1 kg/d)		Seaweed (500 g/d)		Shellfish (100 g/d)		
		Concentration factor	Limit (pCi/litre)	Concentration factor	Limit (pCi/litre)	Concentration factor	Limit (pCi/litre)	
^{3}H	6.6×10^{4}	1	6.6×10^{2}	1	1.3×10^{3}	1	6.6×10^{3}	6.6×10^{2}
^{60}Co	1.1×10^{5}	10^{2}	11	10^{3}	2.2	10^{3}	11	2.2
^{65}Zn	2.2×10^{5}	$10^{3} - 10^{4}$	0.2 - 2.2	10^{3}	4.4	10^{5}	0.2	0.2
^{89}Sr	2.2×10^{4}	1	220	1 - 10	44 - 440	10	220	44
^{90}Sr	8.8×10^{2}	1	8.8	1 - 10	1.8×18	10	8.8	1.8
^{95}Zr	1.3×10^{5}	1	1 300	5×10^{2}	5.2	10^{3}	13	5.2
^{95}Nb	2.2×10^{5}	1	2 200	5×10^{2}	8.8	10^{3}	22	8.8
^{103}Ru	1.8×10^{5}	1	1 800	2×10^{3}	1.8	2×10^{3}	9	1.8
^{106}Ru	2.2×10^{4}	1	220	2×10^{3}	0.2	2×10^{3}	1.1	0.2
^{141}Ce	2×10^{5}	10 - 30	70 - 200	10^{3}	4	10^{3}	20	4
^{144}Ce	2.2×10^{4}	10 - 30	7.3 - 220	10^{3}	0.4	10^{3}	2.2	0.4
^{134}Cs	2×10^{4}	50	4	10	40	10^{2}	20	4
^{137}Cs	4.4×10^{4}	50	8.8	10	88	10^{2}	44	8.8
^{239}Pu	1.1×10^{4}			5×10^{2}	0.44			0.44
^{241}Am	8.8×10^{3}			5×10^{2}	0.30			0.35

a/ICRP value for the public.

b/Lower limit is defined as 1% of concentration of seawater in equilibrium with organisms contaminated at levels with permissible ICRP values.

c/The lowest concentration among those derived from three types of organisms.

Radionuclides: ^{3}H, ^{60}Co, ^{65}Zn, $^{89,90}Sr$, ^{95}Zr, ^{95}Nb, $^{103,106}Ru$, ^{137}Ce, $^{141,144}Ce$, $^{238,239}Pu$, ^{55}Fe, ^{51}Cr, ^{54}Mn

(Ostlund et al., 1969; Palmer and Beasley, 1967; Dutton and Harvey, in press; Wong et al., 1970; Bowen et al., 1971; Hampson and Tennant, in press).

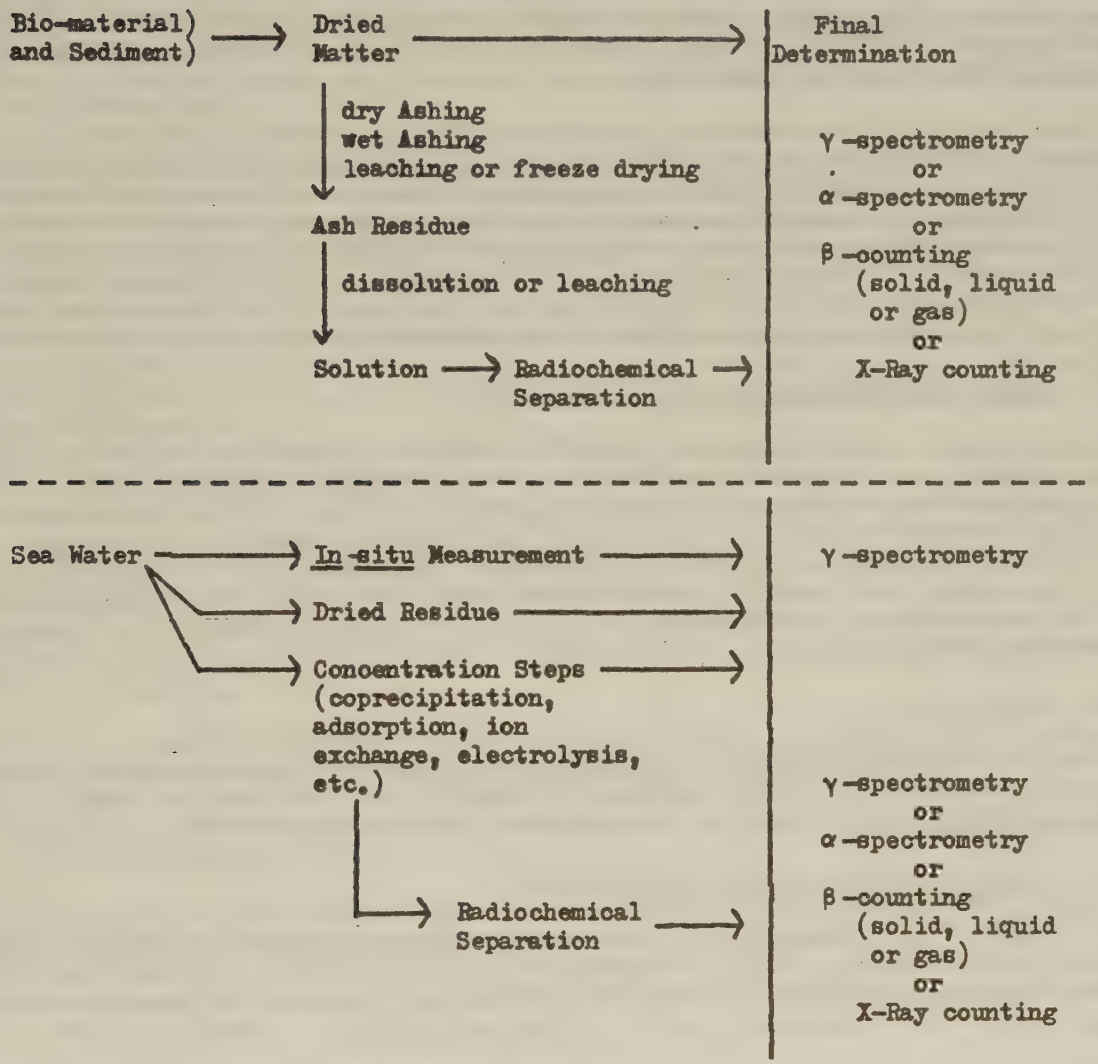

Figure 1: General scheme for radionuclide analysis in a control context (adapted from IAEA, 1970)

For seawater and for bottom sediments *in situ* gamma-spectrometry may sometimes be useful, especially in a control context (IAEA, 1970).

The general scheme given in Figure 1 indicates that gamma-spectrometry can be applied to seawater samples either after evaporation to dryness or after pre-concentration of radionuclides with or without radiochemical separation. Beta-counting may also be applied, where appropriate, after pre-concentratation and/or chemical separations. Bio-material and sediment samples are usually dried or ashed and, if necessary, subjected to radiochemical separations after dissolution or leaching of the ash. The procedures for pre-concentration normally include coprecipitation (Joyner *et al.*, 1967), adsorption (Yamagata and Iwashima, 1963; Gueguéniat, 1967), ion exchange (Carritt, 1965; Riley and Taylor, 1968) and solvent extraction (Joyner *et al.*, 1967). Drying and ashing procedures for bio-material and sediment samples are discussed in detail in sections IV.2.4. and IV.2.5. of "Reference Methods for Marine Radioactivity Studies" (IAEA, 1970).

In cases where pure beta-emitting radionuclides such as strontium-90 have to be identified and quantitatively determined in a mixture of radionuclides or where interfering gamma peaks have to be avoided in gamma-spectrometry, radiochemical separation procedures should be introduced. Although radiochemical separation procedures specific for the radionuclides of interest may be available for the majority of elements, it is important to avoid the introduction of excessively complicated procedures since the time and labour required for the analyses have to be balanced against the value of the information obtained especially in the case of control operations, where undue precision may not be required.

5.3 Design of control programme

It should also be emphasized that effective radionuclide analysis as part of a control scheme can only be achieved on the basis of a well-developed programme which includes the use of pertinent radioecological information, as well as that of hazard assessment. It should also be remembered that the preferable method for radionuclide anlaysis in a control context is the simplest by which the necessary information can be obtained. A scheme for the control of a specific operation must take into account the critical radionuclides, the sensitivity of the apparatus available, the number of samples to be analysed and the personnel available, etc.

5.4 Sample size

Taking the required lower limit of detection for the radionuclides studied (Table IV) and the general sensitivities of the instruments commonly used, the range of sample sizes for seawater is 100 ml to 10 l and for bio-materials and sediments is 100 g to 1 kg.

5.5 Inter-calibration of analytical methods

As a result of a recommendation of the IAEA panel on "Reference Methods for Marine Radioactivity Studies" (IAEA, 1970), the Agency has now implemented a programme for inter-calibration of analytical methods through the distribution of marine radioactivity reference samples.

6. CONCLUSIONS

(a) In the past the major source of artificial radionuclides in the marine environment has been from nuclear weapon testing, some 10^9 curies in the world ocean as at 1970. Contamination has been widespread and except in the vicinity of test areas, low level.

(b) By comparison the contribution from controlled radioactive waste disposal operations has been small, 10^6 curies as at 1970, and the resulting contamination restricted in geographical extent though somewhat higher in concentration.

(c) In the future, assuming that nuclear explosions continue to occur at their present low rate, the major concern with artificial radionuclides in the marine environment will be from the expansion of nuclear power programmes, and the resulting significant but local contamination.

(d) Environmental monitoring requirements for waste disposal operations will be national in character and the present and foreseeable need for global monitoring can be limited to the monitoring of rates of introduction and met by the establishment of an international register of disposals of radioactive waste into the sea (such register to be kept by the IAEA).

(e) Currently available methods for the detection and measurement of artificial radionuclides are adequate for the control of radioactive waste disposal. Future developments will undoubtedly allow for further automation and perhaps, for some radionuclides, *in situ* determination.

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Panel 8: MONITORING ORGANISMS

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1. INTRODUCTION

This material has been prepared to enable the investigator to select bioassay organisms which will be most useful for the detection and evaluation of pollution. Ideally, the selected species or community of different species would reflect not only the presence or absence of specific pollutants but also relative pollution levels and their periodic fluctuations, and perhaps identify factors other than chemical that contribute to environmental degradation. The species selected should be of value in circumscribed geographic locations as well as in larger water areas. Such an ideal type does not exist, of course, and bioassay organisms may be grouped functionally into two general categories as either monitoring or indicator types. The demarcation between these two is not always sharp and there are numerous exceptions to the following generalized definitions.

1.1 Monitoring organisms are used primarily to quantify pollution levels. They possess special characteristics which induce responses that can be measured objectively. Most useful of these measurable responses are the formation of tissue residues of organic and inorganic pollutants, the accumulation of bacterial and viral forms, and the concentration of naturally occurring toxins. Growth rates, fecundity, and viability are easily measured objectively in some organisms and these factors may be useful for monitoring purposes even though they are non-specific as to the type of pollution.

The use of monitoring organisms for the identification and evaluation of pollution levels is hampered by our lack of knowledge of the most sensitive life stages of many otherwise useful species, and by the difficulties involved in identifying sublethal changes. To interpret data derived from field samples, it is necessary to know where the animal has been, what it eats, and what its uptake and flushing rates are for specific pollutants. In the absence of such information, however, many species of plants and animals can be useful if only to identify the presence or absence of persistent polluting substances.

1.2 Indicator organisms, by contrast, are used primarily to identify rather than to measure environmental changes whose cause may be unknown, or which may be the result of a varying mixture of pollutants, for example, industrial effluents. Indicator organisms may be useful in identifying persistent physical changes as well as chemical changes in the environment. Tolerant indicator species may direct attention to pollution because of unusually high population densities. Sensitive indicator species, on the other hand, such as the salmonids, point the finger at pollution by their absence. Changes in species diversity and population density in apparently suitable ecosystems may serve as guides to pollution from a wide variety of sources. Our use of indicator species is hampered by our lack of knowledge of normal fluctuations in most marine communities. Species with planktonic larvae are especially susceptible to "normal" changes in hydrographic features. It is the exception rather than the rule when changes in species composition or population density can be related directly to man-made pollution.

1.3 Test organisms

The utility of both monitoring and indicator organisms is enhanced if they are suitable also as test organisms. Elements of the biota that can be studied under controlled conditions in the laboratory make it possible to interpret and evaluate the importance of field data. They are especially useful in studying the effects of pollutants on animal and plant

behaviour under a variety of simulated field conditions. The most desirable test organisms are small, easy to handle and culture. Euryhaline species are preferable since they can be studied over a broader range of conditions without stress than species restricted to narrow salinity régimes. Species with short life spans are especially useful for studying the effects of sublethal levels of pollution on succeeding generations.

Monitoring organisms must be suitable as laboratory test organisms if the maximum understanding of field data is to be gained. Analyses of tissues from marine mammals, for example, demonstrate the presence or absence of pesticide residues, but there is no way of knowing where or when the residue was acquired or whether it is increasing or decreasing. Periodic sampling of molluscan populations, on the other hand, provides data on fluctuations in pesticide residues in tissues which can be readily interpreted, by extrapolation, since laboratory data on uptake and flushing rates in molluscs are available.

2. SELECTION OF MONITORING ORGANISMS

The choice of a suitable species depends, of course, on the type of information desired. In the context of ocean pollution, we need to know (a) what potentially harmful substances are accumulating in the biota and at what rate, and (b) whether there is evidence of persistent environmental change.

The first consideration in the selection of a monitoring species is its ability to accumulate the pollutants under study without being killed by the pollution levels to be anticipated in the environment. Other criteria are based on the need to know not only existing levels of a pollutant but also its seasonal fluctuations and kinetics in the food web.

The residence time of the monitored organism in the study area should be known reasonably well. This applies, for example, to migrating species of fish and crustaceans which might have acquired tissue residues at some distance from the sampling station.

There should be relatively good understanding of the physiological effects of the suspected pollutants on the monitored species as a result of controlled laboratory studies. Knowledge of the rates at which the organism stores and flushes out residues in relation to the levels of environmental contamination is essential to an adequate interpretation of monitor data.

The organisms should be of convenient size, easily collected, and sufficiently long-lived so that one or more year classes will persist throughout the contemplated monitoring programme. The species should be locally abundant so that its genetic stability and recognized taxonomy may be presumed. There should be sufficient knowledge of the biology of the species to recognize its most sensitive life stage, its position in the trophic web, and its reaction to environmental changes other than those induced by man.

Ideally, monitoring species should have a broad distribution both ecologically and geographically. This condition would be useful in the comparison of data from stations widely separated geographically. Such comparisons must be supported by laboratory data, however, since the assumption of similarities in physiological response on the basis of taxonomic synonomy is unwarranted.

Careful attention must be given to the species trophic position in geographically isolated areas. Food habits are readily modified to suit local conditions. Seatrout, for example, in North American estuaries feed largely on menhaden which because of their high lipid content may have substantial pesticide residues. In some estuaries, seatrout food is made up primarily of crustaceans which typically have very low pesticide residues. The result is that the identical species of fish in adjacent estuaries may present a quite different picture of pesticide pollution levels.

An important consideration in the selection of aquatic monitoring species is their adaptability to handling and transfer from one locality to another. It is frequently desirable to introduce exotic species to determine whether their apparent absence is accidental or caused by pollution. Euryhaline species such as clams and oysters are especially useful in locating sources of industrial pollutants which typically enter the estuary in low salinity areas near river mouths.

2.1 Bacteria

Bacteria are the classical monitors of fecal pollution in the aquatic environment, but many, e.g., E. coli and coliforms are restricted in their usefulness to areas near the source of the pollution. Most bacteria are non-specific in the identification of pollution although a few species, for instance some Salmonella types, may indicate specific industrial wastes. Cl. perfringens is useful in the identification of old and remote pollution, and different Bacillus species may indicate a terrestric, fresh water, or sewage origin of wastes.

One of the advantages of bacteria as indicators is that they may be identified with simple techniques and a large number of samples can be handled at one time. As with many indicators, too little is known about their normal population densities, growth, rates of decay, and dispersion except in fairly localized situations. When monitoring aquatic sites, large samples must be collected frequently, perhaps at daily intervals. Bacterial populations in sediments are more stable, however, and need be checked much less frequently.

A few species are also applied as test organisms in the qualitative estimation of toxic substances in the laboratory.

2.2 Plants - the phytoplankton and macroscopic algae

The heterogeneous nature of plankton communities makes them generally unsuitable for monitoring the environment. Algal blooms, however, are good but uncontrollable indicators of environmental change. Pure phytoplankton cultures are useful as test organisms under controlled laboratory conditions because of their rapid life history. Changes in phytoplankton cell size and division rates are useful in determining the relative toxicities of pollutants under varying conditions in the laboratory.

Macrophytic algae possess several characteristics that qualify them for monitoring the marine environment. The majority are attached so that they reflect water quality at specific locations. Many are large and have a simplified morphology that permits objective measurement of growth rates. Perennial species such as Laminaria hyperborea are useful because their age can be estimated. Drawbacks to their use include the possibility of plants being recruited by water currents from outside the study area, and, as with other marine biota, too little is known about the relative sensitivity of the different life stages and the normal seasonal changes in growth rates.

Many attached species of algae growing at their phytogeographical limits are useful as indicators of thermal pollution or of long term changes in light penetration (turbidity) in the water column.

2.3 Molluscs

The historical and continuing economic importance of shellfish and especially oysters has resulted in a large body of knowledge of their biology. It has been known for a long time, for example, that oysters accumulate metals present in only trace amounts in the environment. This and other information led to an early examination of their ability to accumulate residues of other pollutants, especially the synthetic chlorinated pesticides.

The suitability of oysters and many other pelecypods as monitoring organisms may be briefly described. Pelecypods are sedentary or at least non-migratory; long-lived, up to ten years or more; locally abundant, and some genera have global distribution. The pelagic habit of the larvae has prevented geographic isolation so that the species are genetically stable and taxonomically recognized. Molluscs adapt readily to laboratory culture and can be transplanted to field stations varying quite widely in hydrographic conditions. Their filter-feeding habit places them on a low trophic level and their unusual ability to abstract and concentrate both dissolved and particulate matter from the surrounding water on an almost continuous basis makes them unusually suitable as biological monitors of the aquatic environment.

Laboratory tests have shown that oysters can remove and store DDT, for example, from the ambient water in which the concentration is as low as 0.01 µg/l. They can biologically magnify these residues to levels at least 70 000 times that in the water supply depending on temperature, duration of exposure, and level of contamination. These residues are flushed out of the animal at uniform rates when the water supply is no longer polluted.

The larvae of oysters and clams can be used to indicate pollution levels by determining the percentage of larvae developing normally to the straight hinge stage in a sample of the contaminated water. Although this is a non-specific response, the test has been useful in monitoring pulp mill effluents. The bacteriological examination of oyster tissues is an important tool in monitoring sewage pollution in the marine environment. Visual and olfactory examination of oyster tissues are useful in identifying the presence of excess copper and various petrochemical wastes.

In the United States, clams, mussels, and oysters are routinely used to monitor pesticide and PCB pollution in estuaries. Several species of fresh water clams have been used as monitors in rivers and lakes. A significant use of the mollusc's ability to cleanse itself of pollution in clean water has been the monitoring of commercial shellfish areas contaminated temporarily by fecal organisms or toxins of the naturally occurring paralytic shellfish poisoning. Such programmes are of inestimable benefit in safeguarding man's health while increasing his harvest from the sea.

Knowledge of the ability of oysters to store residues of organic pesticides under test conditions has lead to an analysis of their efficiency relative to other pelecypod genera. The blue or edible mussel appears to be equally suitable as a monitoring organism, and continued evaluation may confirm its usefulness in a global monitoring programme of the marine environment.

2.4 Fish

Fish are frequently used as monitors but from the point of view of protecting man's health or his food resources rather than degradation of the environment *per se*. Consequently, commercial species of fish have been investigated primarily, although others have been examined superficially when they contributed to the food supply of the commercial species. Fish satisfy some of the major requirements of a monitoring organism since many species do accumulate persistent synthetic chemicals and heavy metals. Other species do not tolerate pollutants and avoid contaminated environments thus indicating non-specific contamination. They can be used effectively to measure environmental pollution because so much is known of their basic biology.

Some fish are restricted to well defined geographical areas, water masses, and ecological niches and it is possible to select appropriate species to monitor different seas, water bodies with different temperature and salinity regimes and physical zones of the ocean, i.e., surface, mid-water, or bottom. Other species because of their specialized feeding habits, are helpful in tracing the kinetics of pollutants in the trophic web. The well known migratory pathways of commercial species, both across the oceans and into or out of estuaries and rivers should make it possible to identify the sources of some types of pollutants.

However, the same characteristics may be a drawback to interpreting sampling data when monitoring randomly selected fish populations whose biology is not well known, and little is revealed in such cases about environmental levels of pollution.

Rather little is known of the biology and taxonomy of fish in tropical waters and correspondingly greater care is required there in selecting species suitable for monitoring.

Residue levels in fish are affected markedly by the age of the fish, its lipid content, maturity of ovarian eggs, and state of nutrition. There may also be much individual variation in food habits so that residue levels in fish from the same population and age group may differ by an order of magnitude, and consequently, particular attention has to be attached to the number of individual fish per sample in order to yield statistically satisfactory data.

Many fish species are eminently suitable as test organisms because of their size, availability and short generation time, and eggs and larvae of fish have been used successfully for laboratory testing of response to specific or mixed pollutants. Much progress is being made in assessing the effects of environmental pollution through laboratory studies on the acute effects of one or more pollutants on viability, growth, productivity, behaviour, and of sub-lethal effects on succeeding generations. So far, valuable information is often lacking about the sites of action of the pollutants in the animal and the biochemistry of detoxication processes as well as the tissue levels of the pollutants at the time of death of the test animal.

2.5 Birds

Marine birds frequently represent the top of a food chain. They accumulate persistent, fat-soluble compounds - often at the highest concentrations to be found in the biota. Migratory habits vary considerably, but some species are excellent integrators as they constantly move over large areas. Others remain for several months or half a year at each of two areas in different parts of the world. Some species are geographically restricted throughout their life cycle. The migratory habits of birds are well known compared to most other organisms.

In the studies of contamination with mercury and chlorinated hydrocarbons, bird feathers have been found to reflect the "body burden" of these compounds at the time the feathers were formed. Since feathers are metabolically dead, very small changes in concentrations occur in them as compared to most other tissues. As feathers are formed in a very regular way, knowledge of the pattern of feather formation can make it possible to take a few feathers from a bird with regular migratory habits and, from the residue levels in them, monitor the degree of contamination in various areas of the sea. Accumulation and retention rates of pollutants are more constant and simple to study in bird feathers than in most other tissues monitored. Residue analyses of bird muscle, liver, brain, and development stages, i.e., eggs and nestlings, have also been monitored but these are less satisfactory.

Taxonomically, birds are well known, and populations are easily sampled. To increase the use of birds as monitor or indicator organisms, more information is needed for more species on the pattern of feather formation - the science of ruggology.

2.6 Mammals

Marine mammals, like marine birds, are primarily carnivores and being long-lived tend to accumulate residues of persistent fat-soluble chemicals. Such residues are difficult to interpret since so little is known as to where or when they were acquired. Low residues of DDT (less than 1.0 ppm) reported in sperm whales are predictable, however, since their diet consists primarily of benthic crustacea which tend not to accumulate DDT residues. Conversely, the bottle nose dolphin accumulates residues of up to 800 ppm DDT in its blubber as a result of its diet of coastal fish.

In general, monitoring residues in marine mammals may indicate whether or not the species examined is endangered but will not reflect opportunely the status of environmental pollution.

2.7 Biotic communities

Natural assemblages of bacteria, plant and animal species are sometimes useful as indicators of acute pollution problems or of persistent, more subtle environmental changes.

Changes in communities are revealed by observations on total biomass, numbers of species, and numbers of individuals of a particular species. In some cases morphological change, e.g., reproductive structures in Bryozoa, may indicate specific pollutants. For the most part, however, persistent modifications of the community are non-specific indicators of environmental change.

Despite reasonably good biological information on communal species of polychaetes, molluscs, crustaceans and echinoderms, it is difficult to associate community changes with pollution as opposed to changes resulting from natural factors in the environment. Studies of oyster and barnacle setting rates on test panels over a period of more than two decades, for example, have revealed wide fluctuations in a nominally unpolluted estuary. Nonetheless, test panels exposed during the same periods of time may provide good data for comparing relative water quality at two or more stations in an estuary or coastal lagoon.

Test panels in shallow water are easy to manipulate as non-specific indicators of pollution, but they are exposed to abrupt natural environmental fluctuations. Hydrographic parameters are relatively stable in deep water communities and significant changes are more susceptible to interpretation. For example, divers might be able to associate changes in species diversity at the limits of the euphotic zone on coral reefs with pollution induced changes in water clarity.

3. RESEARCH NEEDS

The small successes attained in earlier and existing monitoring programmes have resulted from the almost intuitive use of biological information gathered for quite different objectives. The currently recognized urgency for monitoring programmes to assess existing levels of pollution as well as to establish base line data banks has exposed the critical gaps in our understanding of some of the most fundamental interactions in the marine ecosystem. If we are to understand and cope with the deleterious changes man is causing in the environment, we must acquire as quickly as possible the biological and technological tools required to measure these changes.

a. The primary research need is for an informed concensus on which components of the biota will be most useful in reflecting objectively environmental contamination and change on a global basis.

b. Obviously, it will then be necessary to assign priorities for contracted research to fill in the knowledge gaps with respect to each of the selected species. Existing data are grossly inadequate on such factors as for example: life histories, most sensitive life stages, physiological response to pollutants, population fluctuations induced by normal environmental changes, trophic webs, and so on.

c. Lastly, it will be necessary to select a circumscribed but reasonably large geographic entity, e.g., the Baltic Sea, in which to evaluate in the field the performance of selected monitoring species and the logistics of monitoring before embarking on the different segments of a permanent global surveillance system.

4. SELECTED REFERENCES

This section presents a brief tabulation of research programmes in which various species have been used satisfactorily for the detection and evaluation of specific types of pollution.

Pollution type	Monitor Group					
	Bacteria	Algae	Molluscs	Fish	Birds	Communities
Municipal sewage	*	*	*			*
Nutrient enrichment	*	*	*			*
Petrochemicals	*	*	*	*		*
Heavy metals			*	*	*	
Other industrial wastes			*	*		
Radioactivity			*	*		
Halogenated hydrocarbons			*	*	*	
Pulp products			*	*		
Heated effluents			*	*		*

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Panel 9: DESIGN OF WORLD MONITORING SYSTEM

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1. DEFINITION OF MONITORING

"Monitoring" is considered to be the systematic observation of properties related to specific problems concerned with the marine environment, the observations being carried out in such a way as to show how these properties vary with time at a number of fixed locations or geographical areas. Its purpose is to show (a) physicochemical and biological changes in the ocean due both to natural causes and the activities of man, (b) changes in marine ecosystems due both to natural causes and the activities of man, (c) the degree of pollution of the ocean. It would therefore require physical, chemical and biological properties to be observed. However, surveys of the abundance of commercially exploited fish stocks are not considered as falling within the framework of a world monitoring system. These stocks are subject to changes in size due to fishing activities and their assessment forms part of the work of the various fisheries commissions of the world.

2. THE CONCEPT OF AN INDIVISIBLE ENVIRONMENT

In designing a worldwide ocean monitoring system it is essential to consider it in relation to similar systems for the atmospheric and the terrestrial environments. The input of certain pollutants to the sea comes from the atmosphere and from the run-off from the land, and it is necessary to assess the magnitude of these inputs and to determine their geographical patterns. Again, primary production in the ocean depends on the amount of solar radiation reaching the sea surface and on nutrient salts, and it is also affected by the degree of mixing in the surface layers, the latter process depending to a great extent on atmospheric conditions. Thus, the monitoring of meteorological and hydrological properties is vital for an understanding of long-term changes in primary production in the ocean. The concept of a total global environmental monitoring system must therefore be adopted. Only by having such an integrated system will it be possible to fully understand the changes that are occurring in man's environment.

3. STRUCTURE OF A GLOBAL OCEAN MONITORING SYSTEM

There are three possible types of monitoring: (1) Local (2) Regional and (3) Global. The global ocean monitoring system can be regarded as consisting of four categories of activity:

3.1 A network of base-line stations

These should be established to follow large-scale changes, particularly of those pollutants that are transported over great distances in the atmosphere or in the sea. They would be in areas where influence from human activities is minimal and in places where they would be typical of a geographical area. Possible sites are mid-ocean islands and oceanic areas in high latitudes.

3.2 A network of impact stations

These should be established to measure the most marked changes and be sited in areas where such changes are likely to be harmful to the marine ecosystem, to food resources and to man. For example, such stations might be sited in major fishing areas, near the mouths of rivers and outfalls transporting large amounts of materials to the sea, and in zones where the transfer of substances from the atmosphere to the ocean is maximal. They should also be sited at critical points along the pathways followed by pollutants through the ocean.

3.3 Remote sensing systems

It appears that remote sensing from satellites might allow some features of the ocean to be viewed on a global scale. For instance, the development of instruments to record the amount of chlorophyll would give an indication of trends in primary production, and the determination of other pigments would allow the frequency of phenomena like "red tides" to be determined. Instruments might also be developed to allow the detection of oil patches and slicks.

3.4 Special systems

These include the use of species to indicate the level of certain pollutants in various geographical areas; for example, wide-ranging species like tuna might be used to give an indication of the level of some pollutants over ocean areas. Bioaccumulators such as algae, molluscs, fish, seals and seabirds and their eggs, that show high levels of pesticides or toxic metals, will have to be used in order to monitor those properties because the detection of their presence and amount in sea water is difficult. Consideration should be given to the use of bioaccumulators at ocean sites by holding them in or on devices attached to buoys, etc. Species of fish and crustacea that are known to be killed or to be sensitive to low level of pollutants might also be used as biological monitors.

Special systems may also be needed to monitor the health effects of coastal pollution, for example. Furthermore, the use of material currently stored in museums may allow the past history of the build-up of certain pollutants to be elucidated, and this could be linked to the trends found at base-line and impact stations.

3.5 National monitoring systems

Some countries already have their own monitoring networks for various pollutants and others will be developed in the future. For example, countries discharging radioactive wastes into the sea have well developed networks that have been operating for a number of years. Again, fish and shellfish tend to accumulate certain pollutants and these may build up to levels at which they are a hazard to human health: the monitoring of stocks of fish and shellfish in order to safeguard against this hazard is a national responsibility. In order to prevent damage by pollutants to the stocks themselves, it is necessary for the countries fishing a particular stock to carry out their own national investigations into the possible effect of various pollutants by acquiring a knowledge of the life history of the stock and of the lethal and sublethal effects of pollutants on (a) the fish at various stages in their life history;(b) the food chain of the fish.

National monitoring schemes mainly fall within our category of Impact Stations. In any global monitoring system they would remain a national responsibility, but it is considered that as far as the data emanating from them are concerned, they should be regarded as part of the world monitoring system.

3.6 Regional networks

It is considered that the global ocean monitoring system will most likely develop from a series of regional networks. In some shelf seas regional monitoring schemes are already coming into being. Some of these are on a bilateral basis, like that for the Gulf of Finland organized by the U.S.S.R. and Finland. Others may be on a multilateral basis, like those at present being discussed for the Baltic and North Seas.

At the same time various worldwide programmes for monitoring certain properties of the ocean and the atmosphere, some including specified pollutants and others not, are in existence or are being discussed. The literature describing these is listed in Section 6 - References. One, or a combination of a number of these, may provide a framework within which a global monitoring system, of the kind with which we are concerned here, can develop.

The development of pilot monitoring networks in selected areas is urgently needed in order to get a better appreciation of the problems involved in running a global system. Such pilot network investigations would best be conducted on a regional basis and the schemes at present being developed for areas like the Baltic and North Seas will be very valuable in this respect and should be given all possible support. Not only will they reveal more about the difficulties involved in developing a global system, but they will lead to improvements in techniques and procedures and give an indication of the costs involved in developing and operating a global monitoring system. The development of these pilot networks should be accompanied by experimental work on a variety of pollution problems.

4. PROBLEMS IN ESTABLISHING A WORLD MONITORING SYSTEM

4.1 The need for an exploratory survey

In designing a global network of base-line and impact stations a considerable difficulty arises on account of our ignorance of the present state of the ocean and its variability. It is not possible to say how best to site the stations or how many there should be. It is therefore recommended that an exploratory survey of the world ocean be carried out at the earliest possible date in order to establish the levels of various substances in the water column, the plankton, the benthos, the littoral zone, the sediments and the fish. Substances that should be surveyed include metals (mercury, lead, cadmium, copper and zinc), polychlorinated biphenyls, petroleum derived hydrocarbons and halogenated hydrocarbons. Consideration should be given by a group of experts as to whether radionuclides should be included or not.

The Study Group on Critical Environmental Problems (SCEP), which met in Williamstown, Massachusetts, in July 1970, has already proposed such a survey and it entails taking 1 000 samples during a one-year survey. It is thought that this survey may be too restricted in its geographical extent and scope.

The plan for the survey should be based on our knowledge of the accuracy of available analytical techniques and of the variability of the ocean. It is clear from a preliminary inspection of the proposed SCEP survey that more stations will probably be required in the northernmost Atlantic and the Mediterranean, Norwegian and Greenland Seas and in upwelling areas. Again the shelf seas, such as the North Sea, are not considered. Nearly as little is known about these areas as the open oceans, yet they are probably the most heavily polluted areas. Such evidence as we have indicates sharp gradients in concentration of some pollutants as one proceeds seaward from the coastal areas, and so closely spaced stations will be needed in these places.

A global monitoring system should sample substances other than those known or believed to be harmful. For example, by monitoring carbon-14 and tritium it should be possible to study the advection-diffusion field of the general circulation of the global ocean. The United States GEOSECS programme, by providing a closely sampled vertical section of geochemical tracers from north to south on the western side of each major ocean basin, is designed to allow such a study and the results of this programme will be helpful in designing the global monitoring network. The proposed exploratory survey, if properly designed, could add to the information collected by the GEOSECS programme.

The proposed SCEP survey calls for 124 fish samples from the fishing areas of the world and a similar number of plankton and benthos samples. In view of the high level of variability found in current monitoring schemes, e.g., that for pesticide residues and metals in fish carried out by the U.K., it would appear that this number of samples is much too small.

4.2 Substances to be monitored

At the present time it is difficult to be precise about the exact range of substances that should be monitored at the stations in the monitoring network. In addition to the usual hydrographic observations (temperature, salinity, dissolved oxygen), observations of nutrient salts, metals, halogenated hydrocarbons, petroleum derived hydrocarbons and polychlorinated biphenyls are proposed.

We discussed this matter with our colleagues from the other Panels at this Seminar and found agreement that lead, mercury, persistent hydrocarbons and petroleum products should be monitored, but no agreement as to priorities. Some members of the Panel propose that carbon-14 and tritium should also be monitored.

Consideration has to be given to sampling for biological parameters which describe the structure and dynamics of the marine biota. In some localized areas, e.g., the littoral zones, biological monitoring can reveal changes in the ecosystem brought about both by natural causes and the activities of man, but in general, because little is known about biological variability in space and time, it is not possible to carry this out at present. It was noted that the U.K. Plankton Recorder Programme is providing valuable information about trends in zooplankton abundance, species diversity and phytoplankton blooms in the North Atlantic and that the present development of an undulating oceanographic recorder for both physical and biological sampling will provide an even more powerful tool. It is urged that consideration be given to using this device for chemical and petroleum sampling as well.

4.3 Frequency of sampling

The frequency of sampling in any monitoring scheme is difficult to decide, again because we know so little about ocean variability. Experimental work and pilot networks will be required in order to establish sampling procedures. A number of moves are afoot to improve our knowledge of ocean variability, for example the Soviet Polygon experiments in the Atlantic Ocean and the Mid-Ocean Dynamics Experiment being discussed by SCOR.

4.4 Standardization and intercalibration

Monitoring schemes that have been carried out to date have shown the need for the standardization of sampling methods and intercalibration of analytical methods. It is suggested that it will be necessary to go a step further in the global case and to divide each sample taken into three parts. The first part would go to laboratories that had been designated as the world reference laboratories for that particular form of analysis; the second part would go to the national laboratory of the country collecting the sample and the third part to an archive so as to be available for examination at a future date if so required.

4.5 Data exchange

There will be a requirement for the free and fullest possible international exchange of data and information collected by a global monitoring system for the oceans. The machinery recommended by the Intergovernmental Oceanographic Commission for the exchange of data seems to be very suitable. Some screening and quality control of data put into World Data Centres will be required and there will be a need for some data to be condensed into the form of means, standard deviations, etc. in order to avoid putting an impossible load on the centres. This especially applies to data coming from regional monitoring systems and national monitoring systems in coastal waters. A data comparison problem may arise when regional networks are combined together if steps are not taken from the outset to intercalibrate methods on a worldwide basis.

4.6 Ship support

It is clear that the demand on ship time of a global network will be large. Consideration should be given to using the weather stations in the North and South Atlantic and the North Pacific as permanent stations in the global scheme and to using the selected ships recruited by national meteorological services in order to collect samples. The U.K. Plankton Recorder Survey shows that merchant ships and weather ships can play an important part in oceanwide monitoring projects. The exploratory survey proposed above should be designed so as to test the suitability of ocean weather stations as stations in a global monitoring system for the ocean and atmosphere.

5. THE ORGANIZATION NEEDED TO ESTABLISH A GLOBAL MONITORING SYSTEM FOR THE OCEAN

The exploratory survey and the global monitoring programme will call for a high degree of collaboration between scientists and between governments. The design of the global monitoring network for the ocean and the scientific evaluation of the data collected lies with the scientific community. The responsibility for running the monitoring system will have to be at governmental level, and here there will be a particular need for very close collaboration, if the ocean monitoring system is to be linked to similar systems for the atmosphere and the terrestrial environment. It is suggested that ways of achieving this might be debated at the UN Conference on the Human Environment which is to be held in Stockholm in 1972. The position of the developing nations should be particularly studied. Their need for the information equals that of the more advanced nations, but the analytical techniques involved in obtaining it are so sophisticated that only the latter possess the appropriate equipment. Consideration should be given to the training of scientists and technicians from the developing countries in marine pollution work and to the provision of suitable laboratories and of sampling analytical equipment within the developing countries so that they can attack their own national problems as well as make a significant contribution to the world monitoring programme.

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Appendix 1

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Appendix 2

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Panel 1: Halogenated hydrocarbons (pesticides and PCB's)

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E. Huschenbeth
S. Jensen
J.E. Portmann

Panel 2: Petroleum

M. Blumer (Chairman)
P.C. Blokker
E.B. Cowell
D.F. Duckworth

Panel 3: Inorganic chemicals (including mercury and lead)

D. Dyrssen (Chairman)
S. Keckes *
C. Patterson
J. Ui
G.F. Weichart

Panel 4: Organic chemicals (particularly with regard to BOD and toxins)

G.G. Widmark (Chairman)
W.D. Garrett
M.P. Nesterova *
K.H. Palmork

Panel 5: Nutrient chemicals (including detergents and agricultural run off)

J.P. Riley (Chairman)
K. Grasshoff
D.W. Menzel *
K. Sugawara *
A. Voipio

Panel 6: Suspended solids and turbidity

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Panel 7: Radioactivity

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Panel 8: Monitoring organisms

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Panel 9: Design of World Monitoring System

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